A
PRE-UNIVERSITY COURSE
OF
CHEMISTRY

A/347

P. K. DUTT

1457

A PRE-UNIVERSITY
COURSE OF CHEMISTRY

(For Pre-university and University Entrance Examinations)

BY

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Admittedly the introduction of three-year degree course in our universities has set up a disequilibrium in the arena of education, and the pre-university course has been conceived as a purely stop-gap measure till to the complete conversion of our secondary schools to the higher secondary stage. It is expected to serve as a link at the transition stage between the secondary schools and the newly adopted three-year degree course. The new situation calls for an adjustment of the course of study and a pre-university course of syllabus in chemistry has been drawn up accordingly. It is in this context that the present volume of 'A pre-University Course of Chemistry' has been published. *It is adapted from the author's 'Text book of Intermediate Chemistry*' which has been abridged to conform to the syllabus of the Pre-university as well as University Entrance Examinations. But at no stage has the continuity of the development of the subject been sacrificed, as the contents of the book will amply bear out. By and large, therefore, it is a short course of chemistry which is complete in itself. In the presentation of the subject matter the author has been largely guided by his experience as a teacher of chemistry for a period extending over twentyfive years, and no pains have been spared to make the book useful to the young learners.

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International Atomic Weights

Name	Symbol	At. no.	At. wt.	Nane	Symbol	At. no.	At. wt.
Actinium	Ac	89	227	Mercury	Hg	80	200.61
Aluminium	Al	13	26.98	Molybdenum	Mo	42	95.95
Americium	Am	95	(243)	Neodymium	Nd	60	144.27
Antimony	Sb	51	121.76	Neptunium	Np	93	(237)
Argon	A	18	39.944	Neon	Ne	10	20.183
Arsenic	As	33	74.91	Nickel	Ni	28	58.71
Astatine	At	85	(210)	Niobium	Nb	41	92.91
Barium	Ba	56	137.36	Nitrogen	N	7	14.008
Berkelium	Bk	97	(245)	Nobelium	No	102	
Beryllium	Be	4	9.013	Osmium	Os	76	190.2
Bismuth	Bi	83	209.00	Oxygen	O	8	16.0000
Boron	B	5	10.82	Palladium	Pd	46	106.4
Bromine	Br	35	79.916	Phosphorus	P	15	30.975
Cadmium	Cd	48	112.41	Platinum	Pt	78	195.09
Calcium	Ca	20	40.08	Plutonium	Pu	94	(242)
Californium	Cf	98	(249)	Polonium	Po	84	210
Carbon	C	6	12.011	Potassium	K	19	39.100
Cerium	Ce	58	140.13	Praseodymium	Pr	59	140.92
Cesium	Cs	55	132.91	Promethium	Pm	61	(145)
Chlorine	Cl	17	35.457	Protoactinium	Pa	91	231
Chromium	Cr	24	52.01	Radium	Ra	88	226.05
Cobalt	Co	27	58.94	Radon	Rn	86	222
Copper	Cu	29	63.54	Rhenium	Re	75	186.22
Curium	Cm	96	(243)	Rhodium	Rh	45	102.91
Dysprosium	Dy	66	162.51	Rubidium	Rb	37	85.48
Eeinsteinium	E	99		Ruthenium	Ru	44	101.1
Eribium	Er	68	167.27	Samarium	Sm	62	150.35
Europium	Eu	63	152.0	Scandium	Sc	21	44.96
Fermium	Fm	100		Selenium	Se	34	78.96
Fluorine	F	9	19.00	Silicon	Si	14	28.09
Francium	Fr	87	(223)	Silver	Ag	47	107.880
Gadolinium	Gd	64	157.26	Sodium	Na	11	22.991
Gallium	Ga	31	69.72	Strontium	Sr	38	87.63
Germanium	Ge	32	72.60	Sulphur	S	16	32.066
Gold	Au	79	197.0	Tantalum	Ta	73	180.95
Hafnium	Hf	72	178.50	Technetium	Tc	43	(99)
Helium	He	2	4.003	Tellurium	Te	52	127.61
Holmium	Ho	67	164.94	Terbium	Tb	65	158.93
Hydrogen	H	1	1.008	Thallium	Tl	81	204.39
Indium	In	49	114.82	Thorium	Th	90	232.05
Iodine	I	53	126.91	Thulium	Tm	69	168.94
Iridium	Ir	77	192.2	Tin	Sn	50	118.70
Iron	Fe	26	55.85	Titanium	Ti	22	47.90
Krypton	Kr	36	83.80	Tungsten	W	74	183.86
Lanthanum	La	57	138.92	Uranium	U	92	238.07
Lead	Pb	82	207.21	Vanadium	V	23	50.95
Lithium	Li	3	6.940	Xenon	Xe	54	131.30
Lutecium	Lu	71	174.99	Ytterbium	Yb	70	173.04
Magnesium	Mg	12	24.32	Yttrium	Y	39	88.92
Manganese	Mn	25	54.94	Zinc	Zn	30	65.38
Mendileirum	Mv	101		Zirconium	Zr	40	91.22

A value given in a bracket denotes the mass number of the most stable isotope.

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A PRE-UNIVERSITY COURSE OF CHEMISTRY

I

SCIENCE AND CHEMISTRY

Science.—Science stands for the sum-total of human knowledge and it extends over the entire realm of nature. It attempts to seek a unity in the diversity of nature, and aims at devising a model of the universe that will explain all that goes on in it, and will also predict its future behaviour. All natural phenomena follow one another in an endless chain of cause and effect. Science gathers facts by observing events in the universe and by collecting results of experiments. Collected in books and in the minds of men, they make the knowledge of our civilisation. *Science is an organised body of facts which have been interrelated and generalised into a system.*

The study of science begins by collecting and comparing facts. When experiments and observations of the same kind yield similar results, it becomes possible to combine them together into general statements, called **laws.** Natural laws may either be discovered by the correlation of experimentally established facts or by making an intuitive guess at some general principles, as to the cause of natural phenomena. Such a speculation is called a **hypothesis.** A hypothesis must not only explain the known facts, i.e., it must be in conformity with the laws, but also predict the discovery of new facts. But when experiments fail to confirm its predictions, the hypothesis is rejected and a new one framed and similarly tested. If the hypothesis survives these tests, it becomes a theory and makes an integral part of the fabric of natural science. A theory in its turn is put to similar tests of predictions and experimental verification. When every fresh finding confirms the theory and proves its truth to the hilt and beyond all reasonable doubt, it is dignified by the name of a law ; but if found wanting, it must either be discarded or modified. A scientific theory is always provisional, but none the less, it stimulates research. Scientific discoveries are but the results of intensive search for new facts and laws, guided by the intelligent use of theories.

Science is a coherent whole and touches all human interest. Natural science has been conveniently divided into different branches for the purpose of study. *Physics* and *Chemistry* belong to the group of physical science which deals with matter and energy without any reference to life. *Botany* and *Zoology*, on the other hand, are different branches of biological science which is concerned with living things and phenomena relating to life process. Other sections of natural science are *Astronomy*, *Geology* and *Physiology*.

Chemistry.—The term chemistry is derived from the word 'chemia', the ancient name of Egypt, which signified a 'divine art' that was highly developed and much practised in the country in the first few centuries of the Christian era. Chemistry as a science is but a recent growth. *The science of chemistry is the study of matter, its properties, composition, and the changes it undergoes.* It is concerned not only with changes in the composition of matter, but also with the gain or loss of energy which accompanies the changes, and the natural laws which govern these changes. The chief branches of chemistry are :

Physical Chemistry which takes note of the scientific laws that govern transformations of matter.

Inorganic Chemistry which is mainly concerned with mineral matter and deals with materials that do not contain carbon. Study of various minerals, metals and non-metals, acids, bases and salts, come under the scope of inorganic chemistry.

Organic Chemistry which is the chemistry of carbon compounds and mainly deals with products of plants and animal origin, viz., proteins, fats and oils, carbohydrates, alkaloids, hormones and vitamins, dyes, etc. Several simple carbon compounds like carbon dioxide, carbon disulphide, etc., are however, treated in both organic and inorganic chemistry.

The science of chemistry has contributed much to improve the life of men. Pottery, porcelain, paper, glass, cement, oils, petrol, paints, varnishes, dyes, plastics, drugs, metals, alloys, etc., which now form the integral parts of modern life, are the gifts of chemical science. Commonplace raw materials have been worked by chemists into many useful things of everyday life. Wood, for example, has been transformed into paper, sugar, artificial silk, and celluloid. It is very often found that waste materials have been profitably utilised by chemists. Coaltar, for example, has been made to yield many brilliant dyes, potent drugs, durable plastics, sweet perfumes, nylon, and saccharin.

New discoveries are always being made and the new applications of old discoveries found for the benefit of the people. The wonder drugs *penicillin*, *chloromycetin* and *streptomycin* are the rich harvests of unremitting chemical research. *Sulpha drugs* are well-known aids in medicine. Planned synthetic chemistry has lifted the veil of nature and has made new substances to order. Some of the milestones are the syntheses of indigo, camphor, cocaine, plant pigments and the red colouring matter of blood. Synthetic rubber and petrol are produced in plenty. The science of chemistry goes a great way to build a sound national economy by proper utilisation of natural resources of a country. It has undoubtedly helped the community to shift from savagery to civilisation. Chemistry supplies the needs of our ever advancing civilisation.

II

FUNDAMENTAL CONCEPTS

Matter.—As we look about, we come across many objects which form the external world around us, differing from each other in size, shape, colour, and such other properties as can be *perceived by one or more of our senses*—touch, sight, hearing, smell and taste. Any one object does not usually affect all our senses, but we see and feel most things. Substances that are invisible may be felt or smelt ; the poisonous sewer gas, for example, may be perceived through the sense of smell ; we feel the presence of air when the wind blows. In general we become aware of the existence of a substance by the sense impressions it produces in our minds. Each kind of substance, that comes to our *senses* in our everyday experience is included in the general term matter. The different kinds of matter that compose the universe are termed *materials.* Each material body has its own distinguishing characteristics, otherwise called it *properties*, by which it can be recognised or identified and separated from other materials. Sugar is one material, iron is another, glass another. One may identify a white substance as sugar, if it is sweet. Sweetness is one of the properties of sugar. Iron has the property of rusting in moist air ; glass the properties of brittleness and transparency. These differences in essential properties are due to the fact that *substances may differ in composition. Difference in composition of various kinds of matter gives rise to difference in properties.* Sugar and salt are two materials of different composition and hence they differ in many of their properties. These differences exist, quite apart from any particular size or shape of the materials. A lump of sugar and powdered sugar are but two different forms of the same material. To alter its sweetness, it must be transformed into something else which is not sugar, i.e., into a different substance.

A substance retains its specific properties so long as its composition remains the same. Various material substances may differ in their essential properties, but all of them occupy some *space* and possess some *weight*, and what is called *inertia* by virtue of which a substance requires a *force* to set it in motion, and if already in motion, to alter the motion. Air, earth, water, rock, wood, glass and iron are a few familiar forms of matter.

Matter possesses mass (which we measure by weight) and occupies space and may be perceived through one or more of our senses.

Three States of Matter.—Matter may exist in three states, *viz., gas, liquid and solid.* Matter in the gaseous state possesses the property of filling completely and uniformly any available space. A gas is characterised by its lack of definite shape or volume. It assumes the shape of the containing vessel which it fills completely and to a uniform density. Hydrogen, oxygen, nitrogen, and carbon dioxide are examples of gaseous substances. Matter in the liquid state possesses no shape of its own ; it takes the shape of the vessel in which it is contained, but it does always retain a definite volume. Solids are distinguished by having sufficient rigidity to maintain a definite shape. A substance in the solid state has got a definite shape and size of its own. A piece of wood will always have the same shape and will always occupy the same space.

Physical and Chemical changes.—Matter undergoes two kinds of changes. Many changes take place which do not affect the composition of a substance ; these are referred to as physical changes. A change that affects the composition of a substance is known as a chemical change. Examples are :

(i) A lump of sugar, if broken to pieces, still remains sugar ; the powdery sugar tastes as sweet. But when strongly heated, it loses its colour and sweetness and chars into a black mass which is not sugar, i.e., the composition of sugar has been altered. Sugar is said to undergo a physical change in the first instance and a chemical change in the second case. When sugar dissolves in water, it undergoes a physical change, since it is not chemically changed in being dissolved. It retains its sweetness even in solution. The whole amount of sugar may be recovered, unchanged in mass and composition, on evaporating the solution to dryness.

(ii) On dropping a few crystals of iodine in a heated flask, the latter is filled with violet vapours of iodine ; this is a physical change.

(iii) When a piece of iron *rusts* in moist air, it becomes coated with a *reddish brown* powder. During rusting iron has combined with the oxygen of air, forming a new substance, called iron oxide, which is the rust. Iron + oxygen = iron oxide. This is a chemical change.

(iv) When a piece of steel is magnetised, its colour, density, tenacity, mass, and the composition (and hence the chemical properties) remain unaltered. This is a definite physical change. The change is easily reversed on heating.

(v) A piece of platinum becomes white-hot on heating and emits light. It is, however, restored to the original state on cooling. This is another example of a physical change.

(vi) When water is heated until it vaporises, it becomes steam. But the steam becomes water again on cooling, and hence it is the same substance as water. The vaporisation of water is a physical change. Again, cooling freezes water into ice ; ice melts into water when heat is applied. Ice, water and steam are but different forms of the same substance, and all of them have the same composition, and hence the same chemical properties. The transformations of water into ice and steam are undoubtedly physical changes.

$$\text{Ice} \underset{\text{cool}}{\overset{\text{Heat}}{\rightleftharpoons}} \text{water} \underset{\text{cool}}{\overset{\text{Heat}}{\rightleftharpoons}} \text{steam}$$

(vii) When a piece of magnesium is burnt in air, it gives a blinding white light—the ash that is left is different from the magnesium in its properties. Like magnesium, it does neither burn nor does it liberate hydrogen from dilute sulphuric acid. The ash weighs more than the magnesium that was burnt, since during combustion the latter has combined with the oxygen of air producing the ash which is magnesium oxide and is white in appearance. This change takes place with evolution of heat. This is a chemical change.

Magnesium+oxygen=magnesium oxide.

The white magnesium oxide when strongly heated in air, glows with a bright light. On cooling there is no change in the substance. The glowing is a physical change.

(viii) When a piece of clean copper wire (rose-red in colour) is heated in a Bunsen flame, it colours the flame green. The heating is continued unitl it no longer gives any green colouration. It has now turned black due to its conversion into a new substance, called copper oxide. This is a chemical change.

Copper+oxygen = copper oxide.

(ix) When water is sprayed on to a lump of quick lime, the latter crumbles to powder with a hissing noise and evolving much heat. Quick lime has become slaked lime by combining with water. This is a chemical change.

Quick lime+water = slaked lime.

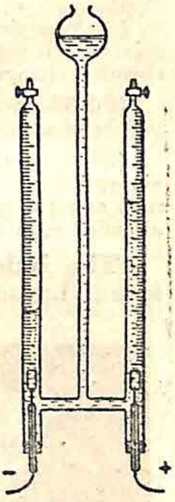

FIG. 1

(x) **Electrolysis of water.**—When an electric current is passed through water, *acidified with dilute sulphuric acid*, it is decomposed into two new substances hydrogen and oxygen. This is obviously a chemical change. Since water is a bad conductor of electricity, it is acidified with dilute sulphuric acid before electrolysis. The electrolysis is carried out in an apparatus, called a voltameter (fig. 1) ; it consists of three glass tubes—the central one carrying a funnel acts as a reservoir of water, and the two graduated tubes at the bottom of which are fused two platinum foils are the collecting vessels. The voltameter is filled with the acidulated water through the funnel, and the two platinum foils are connected to the negative and positive poles of a battery. On passing the electric current, bubbles of gas rise from each electrode and collect into the two side tubes—the volume of the gas at the negative electrode, called the **cathode,** is twice that of the gas at the positive electrode, known as the **anode.** The gas liberated at the cathode, burns with a pale blue flame, and is known as hydrogen ; the gas that is liberated at the anode, rekindles a glowing chip of wood, and is called oxygen. Thus, *water is decomposed by electrolysis into two volumes of hydrogen and one volume of oxygen.*

(xi) *Decomposition of mercuric oxide.*—When red oxide of mercury, also called mercuric oxide, is heated in a test tube, the colour changes to back, but on cooling the red colour of the substance is restored. No change has occurred in the mercuric oxide itself ; this is a physical change. But when strongly heated the mercuric oxide breaks up into two new substances mercury and oxygen :

Mercuric oxide=mercury+oxygen

A shining mirror of mercury is deposited on the upper part of the tube. A glowing splint held at the mouth of the tube, is rekindled showing that a gas, called oxygen, is given off. This is a chemical change.

(xii) When pellets of mercuric thiocyanate are ignited by the flame of a taper, they burn, swelling into a curious worm-like structure, the so-called **Pharaoh's Serpent.** This is a chemical change.

Characteristics of physical and chemical changes.—Some of the main characteristics of physical and chemical changes are :

(i) A physical change alters only the physical properties of matter. Physical properties of matter include the familar properties directly perceptible to our senses, such as colour, odour, taste, size, shape, etc. which may be observed without transformation into new substances. *No new substance is produced in a physical change.*

A chemical change alters the specific chemical properties of a substance. The chemical properties of a substance are related to its capacity for being transformed into substances of other kinds. *New substances with different properties are produced in chemical changes.* Chemical changes are always accompanied by physical changes.

(ii) A physical change is usually *temporary*, and can easily be reversed by appropriately altering the external conditions such as pressure and temperature ; the chemical change, on the other hand, is permanent and cannot be easily reversed.

(iii) The weight of a substance remains unaltered in a physical change ; the weight of a material usually alters when it is transformed into a new substance.

(iv) A physical change is not usually accompanied by marked evolution or absorption of heat, except when the latent heat is absorbed in the change of state such as melting and evaporation ; a chemical change, on the other hand, is always attended with either evolution or absorption of heat.

The indestructibility of matter.—In 1774 the great French savant Lavoisier put forward the law of conservation of mass which forms the basis of all quantitative works in chemistry. Matter can undergo changes or what are called transformations from one form into another. But the law states that :

The mass of a system remains unaltered by any change that takes place within it. In other words, *matter can neither be created nor destroyed. There is*, therefore, *no change in the total mass of matter when a chemical change occurs*, i.e., the total mass of matter before the change is equal to the total mass of matter after the change. Hence, within limits of experimental errors, the sum of the weights of the products must be equal to that of the weights of the reactants in a chemical reaction. In other words there can be no gain or loss of matter accompanying a chemical change. Thus, when a certain weight of mercuric oxide, say 15

Antoine Laurent Lavoisier (1743-94)
FIG. 2

grams, is completely decomposed by strong heat into mercury and oxygen, the total weight of mercury and oxygen must also be 15 grams :

Mercuric oxide = mercury+oxygen

∴ wt. of mercuric oxide=wt. of mercury+wt. of oxygen.

The above principle is usually referred to as *the law of conservation of mass*, or *the law of indestructibility of matter*, since the weight is proportional to mass, which measures the quantity of matter.

Illustrations : (i) **Lavoisier's experiment.**—Lavoisier was the first to explain and establish the law of conservation of mass. In one of his experiments he heated a piece of tin in a SEALED retort containing air, when a part of tin was calcined into its oxide. The apparatus was weighed before heating and was allowed to cool after heating and weighed again. *No change in weight* was found, proving that there was no loss or gain of matter during the calcination of tin which was a chemical change.

(ii) **Charcoal Experiment.**—When a piece of charcoal is ignited, it continues burning and finally disappears completely. This simple experiment suggests an *apparent* loss of matter. But this is actually not the case. The piece of charcoal unites with the atmospheric oxygen during burning, forming carbon dioxide gas which passes into the atmosphere, and hence the apparent loss of matter. But if the weight of oxygen used up is taken into consideration, there would occur no loss or gain in weight as the charcoal burns—the sum of the weights of charcoal and oxygen would be found to be equal to the weight of carbon dioxide formed.

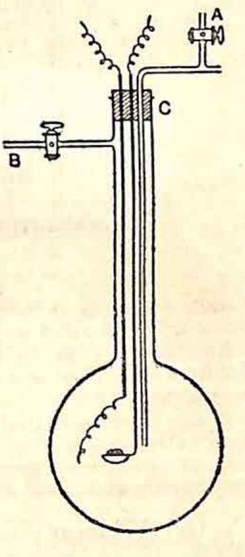

Fig. 3

The following experiment on *combustion of charcoal* clearly demonstrates it. A piece of charcoal is burnt in oxygen in a closed space so that no material can escape. A round-bottom flask (fig. 3) is provided with a tightly fitting rubber-stopper, through which pass two copper wires. One of the wires carries a spoon on which a piece of charcoal rests. A platinum wire, touching the charcoal, joins the two copper wires. The flask is filled with oxygen —the tubes A and B are meant for filling the flask with oxygen, and then carefully weighed in a balance. The two copper wires are then connected to the two terminals of a battery, and an electric current is passed through the platinum wire which becomes red hot and ignites the charcoal. The current is passed until the charcoal disappears completely with the formation of carbon dioxide :

Charcoal+oxygen = carbon dioxide

The battery is then disconnected, and the flask is cooled and weighed again. The weight is found to be the same as before. Hence matter is neither created nor destroyed during the transformation of charcoal into carbon dioxide.

(iii) **Candle Experiment.**—When a candle burns in air, it gradually disappears, leaving hardly anything. There is thus an *apparent* loss of matter. But actually the material of the candle which is wax, is not lost on combustion. It is changed into two gaseous substances, carbon dioxide and water vapour, which escape into the atmosphere, and hence the apparent loss in weight. But it may be shown that the products of the change, i.e., carbon dioxide and water vapour, weigh more than original candle itself, since a part of air (which is oxygen) is used up when the candle burns. If however, a proper balance sheet is drawn up, it would be seen that the weights of materials used up on one side and those formed on the other do exactly balance : Candle+oxygen = carbon dioxide+water vapour.

In the candle experiment a small candle is placed on a perforated cork (to admit air) at the bottom of a glass chimney, the top of which is connected with a U-tube containing pieces of caustic potash in one limb and fused calcium chloride in the other. The chimney with the U-tube is carefully weighed in a balance. Then the U-tube is connected on the other side with an aspirator full of water (fig. 4). The candle is now lighted and quickly replaced, and the water is allowed to run out of the aspirator when air enters the chimney through the perforations in the cork. The candle continues to burn in the draught of air caused by the suction in the aspirator. After a few minutes the tap of the aspirator is turned off and the candle goes out. The chimney with the U-tube is then cooled and weighed again. It is found that far from a *loss* of weight occurring when the candle burns there is actually an increase in weight. This increase in weight is not, however, due to any creation of matter but due to the fact that the matter which is the candle, instead of being destroyed during burning, has united with the oxygen of air to form carbon dioxide and water vapour which have been absorbed by the caustic potash and the calcium chloride respectively and hence the increase in weight.

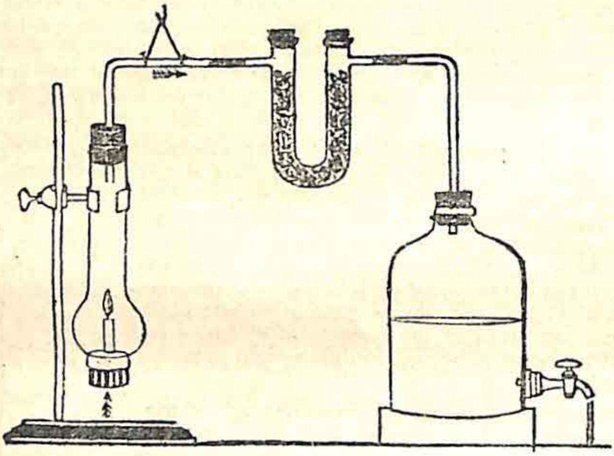

Fig. 4

(iv) When a piece of iron rusts in moist air, it increases in weight. There is an *apparent* creation of matter in this instance. But the gain in weight is due to the fact that a part of air which is oxygen, is used up in the rusting of iron. The total weight of the iron and oxygen used up is, however, equal to that of the rust formed which is iron oxide : Iron+oxygen = iron oxide.

(v) Similarly, when a piece of magnesium ribbon is heated in air, it burns away to a white powder, called magnesium oxide, which weighs more than the original magnesium. It appears to violate the law of conservation of mass. The gain in weight of magnesium when it burns is equal to the oxygen of air used up. Hence the total weight of magnesium plus the oxygen used up is equal to the weight of magnesium oxide produced :

Magnesium+oxygen = magnesium oxide.

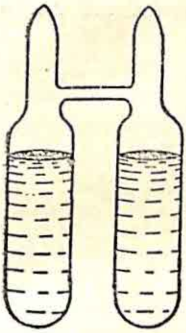

FIG. 5

(iv) **Landolt's Experiment.**—The law was put to the most rigid test by Landolt between the years 1899 and 1906. In one of his experiments, the reacting materials, e.g., *ferrous sulphate* and *silver sulphate* solutions, in the two arms of an H-tube (fig. 5), was sealed off. It was then weighed very accurately. The solutions were mixed together by tilting the tube, when the reaction took place—the silver sulphate was reduced to metallic silver by the ferrous sulphate. The reaction over, the tube was allowed to cool for some time and weighed again. It was found to weigh the same as before. Hence the truth of the law.

Similar experiments can easily be carried out in the laboratory. In one experiment, some ferric chloride solution in a test tube is placed in a conical flask containing potassium ferrocyanide solution. The flask is then corked and weighed. The two solutions are mixed together by tilting the flask, when a deep blue precipitate forms. There is, however, no change in weight. The experiment may be repeated with solutions of mercuric chloride and potassium iodide ; on mixing the two solutions a yellow precipitate (which rapidly turns red) of mercuric iodide is produced—the precipitate,however, dissolves in an excess of potassium iodide solution.

The Law of Conservation of Energy.—Very much like matter, energy may be transformed from one kind to another without any gain or loss in the total amount of energy in the universe, i.e., *energy can neither be created nor destroyed:* but unlike matter, it possesses no weight nor does it occupy any space. The energy of a body may be defined as its power to perform work. Heat, light, electricity, motion, etc., are the familiar forms of energy. Whenever one form of energy disappears, an equivalent amount of energy of other kind or kinds must appear. Heat under the boiler generates steam which drives the engine. The engine produces motion which is utilised in running a dynamo. The dynamo generates electric current which may turn a motor.

Matter cannot undergo any change by itself ; the change is brought about by energy. Natural phenomena are nothing but manifestations of interplay between matter and energy.

Exothermic and endothermic changes.—The chemical changes which matter undergoes are almost always attended with more or less marked changes in energy, which usually manifests itself with the evolution or absorption of heat. The chemical changes which take place with evolution of heat are known as **exothermic changes,** while those taking place with absorption of heat are referred to as **endothermic changes.**

Compounds, such as carbon dioxide, water, hydrogen chloride etc., which are formed from their elements with evolution of heat are known as **exothermic compounds.**

When sulphur vapour passes over red-hot charcoal, a colourless liquid, called carbon disulphide, is formed. Its formation takes place with absorption of heat which is contained in it. Hence carbon disulphide contains more energy than its constituent elements. Compounds, such as carbon disulphide, nitric oxide, and hydriodic acid, etc., which are formed from their elements with absorption of heat are known as **endothermic compounds.**

Varieties of matter.—Although there are a vast number of different chemical substances, it is now realised that there are only * ninety-two distinct species from which these numerous substances are composed. The simple species or types of matter are called

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*There are ninety-two (taking the elements beyond uranium, namely, neptunium, plutonium, americium, curium, berkelium, californium, einsteinium, fermium, mendelevium, and nobelium, into account, the number is one hundred and two) elements but not a few of them are very rare—some are no more than laboratory curiosities.

elements. Various forms of matter are classified into elements and compounds according to their composition.

The era of modern chemistry begins with Robert Boyle who in the seventeenth century clearly distinguished elements as '*substances which cannot be decomposed further*.'

Element.—*An element may be defined as a substance which cannot be decomposed into any simpler substances by means of ordinary chemical reactions.*

Magnesium is an element. It cannot be decomposed into anything simpler than magnesium. A piece of magnesium ribbon, weighing about 0.5 grams, is slowly heated in a loosely covered porcelain crucible (fig. 6) till combustion is complete. The crucible is then heated strongly for some time, cooled, and weighed. There is an increase in weight. The magnesium has combined with oxygen from the air to form magnesium oxide, which is a white powder :

Magnesium + oxygen = magnesium oxide.

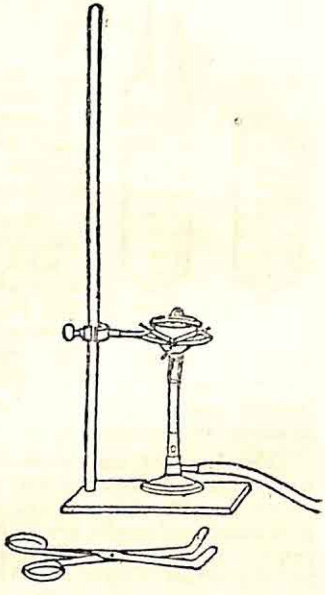


FIG. 6

If the magnesium were decomposed into simpler substances, the white powder and something else, the white powder would have weighed less than the magnesium. But the white powder weighs more, and hence the magnesium has become something more complex by taking oxygen from the air. *We can, therefore, add to an element, but we cannot decompose it.*

Copper, silver, gold, iron, tin, lead, magnesium, aluminium, carbon, sulphur, hydrogen, oxygen, nitrogen, etc., are few familiar elements.

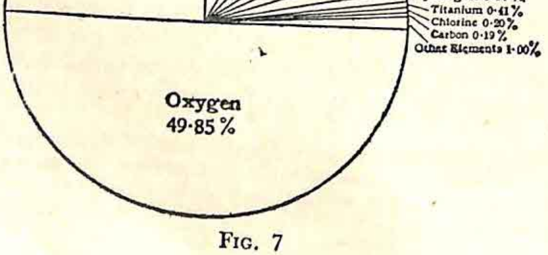


FIG. 7

Oxygen alone makes up about half of the weight of earth's crust, eight-ninths of the ocean, and about a fifth of the atmosphere.

The distribution of elements in the earth's crust is shown in the following diagram (fig. 7). The elements vary greatly in relative abundance. Oxygen, silicon, aluminium, iron, calcium, sodium, potassium, and magnesium are the eight most common elements which make up about 97 per cent of earth's crust, the ocean and the atmosphere.

Compound.—*A compound may be defined as a substance which is formed by the chemical union of two or more elements in a definite proportion by weight, and consequently a compound may be separated into two or more elements.*

Compounds may either exist in nature or have been prepared in the laboratory. Mercuric oxide, also called red oxide of mercury, is a compound, as it breaks up into mercury and oxygen by strong heat.

About 2 grams of mercuric oxide are taken in a hard glass test tube (fig. 8) fitted with a rubber stopper through which passes a glass delivery tube leading to a pneumatic trough containing water; a gas jar full of water, is inverted in the trough—the mouth of the jar being supported on a beehive shelf over the delivery tube. The test tube is clamped in a horizontal position. On heating the mercuric oxide, bubbles of gas collect in the jar, and at the same time a shining mirror of mercury deposits on the cooler part of the tube. The gas rekindles a glowing chip of wood, which burns with a brilliant flame, indicating that the gas is oxygen : Mercuric oxide=mercury+oxygen.

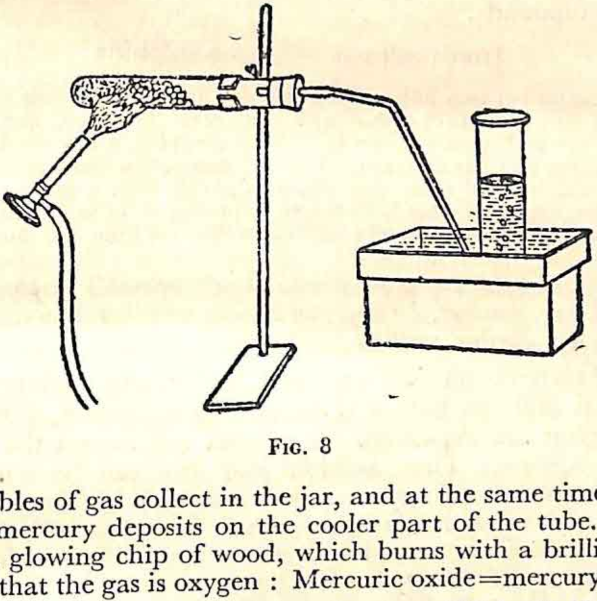


FIG. 8

When an electric current is passed through water acidified with dilute sulphuric acid, it decomposes into hydrogen and oxygen, indicating that water is a compound. Fused common salt may be decomposed into sodium and chlorine by passing electric current through it.

Mixture.—*A mixture, sometimes called a mechanical mixture, is obtained by the mere blending, without any chemical union whatsoever, of different substances (elements or compounds), which are easily identified in the mixture by their respective properties which remain unaltered.*

The gun-powder is an intimate mixture of three materials, nitre, also called potassium nitrate, charcoal, and sulphur. Air is a mixture of nitrogen and oxygen mainly.

Mixtures and compounds.—A mixture differs from a compound in the following respects :

(i) *The components, or what are called the ingredients, of a mixture retain their specific properties ; a compound, on the other hand, possesses properties which are peculiar to itself alone and are entirely different from those of its components.*

A mixture of 7 grams of clean fine iron filings and 4 grams of flowers of sulphur is heated in a test tube, when the whole mass glows—the change takes place with evolution of much heat. When cold, the tube is broken in a mortar, and the resulting black mass is powdered. When the powder is examined under a lens, no particles of sulphur or iron are visible in it, although these can be seen in the mixture. When a magnet is brought before the new substance no iron is attracted, as it is from the mixture. Carbon disulphide, a liquid that dissolves sulphur, does not dissolve out any sulphur from the new substance. Hence iron and sulphur have disappeared as such forming a new substance, called ferrous sulphide, which is a chemical compound :

$$\text{Iron} + \text{sulphur} = \text{ferrous sulphide}$$

When a mixture of iron filings and sulphur is treated with dilute sulphuric acid, a gas is given off which burns with a pop. The gas is hydrogen, and is formed by the action of the acid upon the iron filings. The sulphur is not attacked and is left over when all the iron has dissolved. When, however, the iron sulphide, also called ferrous sulphide, is acted upon with dilute sulphuric acid, a gas is evolved which smells of rotten eggs. The gas is hydrogen sulphide ; it burns but not with a pop. These experiments show that ferrous sulphide is different from both iron and sulphur in properties.

(ii) *The components of a mixture are easily separable by physical means ; a compound may, however, be separated into its constituents by chemical means, but not by any physical method.*

If a mixture of iron and sulphur is shaken with carbon disulphide, and filtered and the filtrate is allowed to evaporate, yellow crystals of the sulphur are deposited. A magnet can attract the iron filings from the mixture. Thus, sulphur and iron can be removed from the mixture by physical means. But it is only by chemical methods that iron and sulphur can be obtained from iron sulphide. Thus, when iron sulphide is treated with dilute hydrochloric acid, hydrogen sulphide (a gas which smells of rotten eggs) evolves ; if it is burnt in air and a cold crucible lid is held in the flame, sulphur is deposited.

(iii) *The composition of a mixture is variable but the composition of a compound is fixed and definite.* Fixed composition is one of the best tests for a compound.

In whatever way the iron sulphide is preapred it must always contain 7 parts of iron to 4 parts of sulphur. When more iron than what is required by this proportion is heated with sulphur, the excess iron remains over, mixed with iron sulphide, and can be removed from it with a magnet. When an excess of sulphur is used, it does not combine ; it burns away or remains mixed with iron sulphide from which it can be dissolved out with carbon disulphide.

(iv) *Heat is either evolved or absorbed during the formation of a compound from its elements ; but when a mixture is made there is usually no heat change.*

Much heat is evolved during the formation of iron sulphide, but not when iron filings and sulphur are merely blended together. Heat change sometimes accompanies the formation of a solution which is a mixture, e.g., much heat is absorbed when ammonium chloride is dissolved in water ; when water is added to sulphuric acid the solution becomes extremely hot.

✓(v) *A mixture is usually heterogenous i.e., not perfectly uniform whereas a compound must be always homogeneous, i.e., the same throughout.*

This criterion obviously does not hold for solutions which are perfectly homogeneous mixtures. A magnifying glass reveals distinct particles of iron filings and sulphur in their mixture, but not in iron sulphide.

(vi) *A compound has fixed melting and boiling points, whereas a mixture usually has no definite melting or boiling point.*

A Homogeneous Substance is one in which every part of the substance has exactly the same composition and properties as every other part. Crystals of copper sulphate, common salt, etc., are homogeneous bodies. A compound *must* be homogeneous, since it contains only one kind of substance.

A Heterogeneous Substance exhibits different properties in its different parts. Gun powder is a heterogeneous mixture of nitre, sulphur and charcoal. A heterogeneous substance must be a mixture.

Metals and non-metals.—The elements are divided into two main classes, viz., *metals and non-metals*, on the basis of their properties. The classification, though convenient, is somewhat arbitrary, since their properties sometimes overlap. Thus, there are elements which exhibit more or less the properties of both metals and non-metals, they are referred to as *metalloid.*

Potassium, sodium, calcium, magnesium, aluminium, zinc, iron, tin, lead, copper, mercury, silver, platinum, and gold are some of the familiar metals. Hydrogen oxygen, nitrogen, phosphorus, fluorine, chlorine, bromine, iodine, carbon, silicon, boron, and sulphur are examples of non-metals. Arsenic and antimony are metalloids.

The main features of difference in properties between metals and non-metals are :

Physical differences

METALS	NON-METALS
1. Metals possess *lustre*, called *metallic lustre* and *reflect light* from polished or freshly cut surface.	Non-metals have *no lustre* (except graphite and iodine which are lustrous) and *do not reflect light.*
2. Metals usually *have high densities* with several exceptions ; lithium, for example, is a light metal with a density of 0.53 only ; sodium, potassium, calcium, magnesium and aluminium also have low densities. Metals with densities greater than 5 are called *heavy metals*—osmium with a density of 21.3 to 24 is the heaviest.	Non-metals have *low densities*, all below 5—liquid hydrogen, density 0.076, is the lightest, and iodine with a density of 4.93 is the heaviest.

3. Metals are usually *good conductors of heat and electricity.* Silver is the best conductor ; copper is the next best. Mercury is not a very good conductor.	Non-metals are *poor conductors of heat and electricity* except graphite. Arsenic has also marked conductivity.
4. Metals possess *tenacity* and *toughness*, i.e., possess resistance to rupture by a stretching force and twisting respectively. Metals also possess *malleability* and *ductility*, i.e., possess the property of being hammered into thin sheets and drawn into wires respectively. Some metals, e.g., bismuth and antimony, are brittle. Gold is the most malleable metal—gold leaf 1/280000 of an inch in thickness may be made by hammering.	Non-metals possess none of the properties of tenacity, toughness, malleability and ductility—non-metals are brittle, if solid.
5. Metals are *solids* with the exception of *mercury* which is a liquid at the ordinary temperature.	Non-metals are usually *gases*, or *volatile solids* or *liquids ;* thus amongst the members of halogen family, fluorine and chlorine are gases, *bromine is a liquid*, and iodine a volatile solid. The non-metals carbon, boron and silicon are non-volatile solids.

Chemical differences

METALS	NON-METALS
1. Metals are *electropositive* elements (i.e., they carry positive charges during electrolysis) ; in other words, they form *cations*, e.g., $ZnCl_2 \rightleftharpoons Zn^{++} + 2Cl'$. Metals may sometimes form part of complex anions, e.g., $KAg(CN)_2 \rightleftharpoons K^+ + Ag(CN)_2'$.	Non-metals are *electro-negative* elements, i.e., they form *anions* (i.e., they carry negative charges during electrolysis), or hardly show any electrochemical character, e.g., carbon. Hydrogen though a non-metal, is generally electro-positive and forms a cation, e.g., $HCl \rightleftharpoons H^+ + Cl'$
2. *Metals generally dissolve in HCl or dilute* H_2SO_4, giving off hydrogen—metals which are less electropositive than hydrogen are, however, exceptions.	Non-metals *do not dissolve in* HCl or dilute sulphuric acid.
3. Metal usually form *basic oxides*, e.g., CuO, Fe_2O_3, CaO, but some oxides such as ZnO, and Al_2O_3 are amphoteric ; some metallic oxides of higher valency are, however, acidic, e.g., CrO_3 and Mn_2O_7.	Non-metals form *acidic oxides*, e.g., SO_2, CO_2, P_2O_3 ; some oxides such as N_2O, NO, CO, etc., are neutral.
4. Metals form *halides* which are *stable in presence of water*, e.g. $NaCl$, $CaCl_2$, etc., but some are partially hydrolysed i.e., decomposed by water—the hydrolysis is *reversible*, e.g., $FeCl_3 + 3H_2O \rightleftharpoons Fe(OH)_3 + 3HCl$ Metallic halides are mostly non-volatile, and conduct electric current in solution in water. Stannic chloride, $SnCl_4$, is a volatile liquid, and a non-electrolyte.	Non-metals form *halides* which are usually *unstable towards water*,—most of them are decomposed by water ; the decomposition is *irreversible :* $PCl_3 + 3H_2O = H_3PO_3 + 3HCl$. Carbon tetrachloride, CCl_4, is stable towards water.
5. Metals generally form *complex salts* in which the metal may be in the *cation*, e.g., $[Cu(NH_3)_4]SO_4 \rightleftharpoons [Cu(NH_3)_4]^{++} + SO_4''$ or in the anion $K_4[Fe(CN)_6] \rightleftharpoons 4K^+ + [Fe(CN)_6]''''$	Non-metals *do not usually form complex salts ;* boron and silicon, however, may form complex fluorides, e.g., KBF_4 and K_2SiF_6

The constitution of matter.—Mass of a body is the matter contained in it, but what constitutes a mass of matter? Several Greek philosophers, over 2,000 years ago, suggested that all kinds of materials in the universe, however continuous they may appear to be, are composed of very minute particles, called **molecules,** which are much too small to be perceived individually.

Molecule.—*A molecule may be defined as a smallest particle of an element or a compound which can exist in the free state. A molecule possesses the chemical properties of a given type of matter.*

According to the atomic theory put forward by Dalton in 1803, an element is assumed to consist of extremely minute particles called **atoms.** The atom of each element has a characteristic weight.

Atom.—*An atom may be defined as the smallest particle of an element which can take part in a chemical change.*

Molecules are composed of atoms. The smallest unit of a compound is a molecule; this can exist as such in the free state. With an element it is necessary to distinguish between atoms and molecules, because the atom may not be always capable of any prolonged existence in free state. In the case of inert gases of the atmosphere, viz., helium, neon, argon, krypton and xenon, and vapours of most metals, mercury for example, the atom is capable of free and independent existence. For these elements, therefore, the atom and the molecule are identical. *Usually, however, two or more atoms compose a molecule of an element.* The molecules of the common gases hydrogen, oxygen, nitrogen, and chlorine contain two atoms, and the molecules of phosphorus and arsenic contain four atoms.

A molecule of an element contains like atoms only. A molecule of a compound is composed of atoms of the different elements making the compound. An element, therefore, is a substance that consists of atoms of one kind only; a compound is a substance that consists of atoms of two or more different kinds. Since a compound has a definite composition, a molecule of compound must contain a fixed number of atoms.

For example, a molecule of water consists of 2 atoms of hydrogen and 1 atom of oxygen; a molecule of sulphuric acid contains 2 atoms of hydrogen, 1 atom of sulphur, and 4 atoms of oxygen; a molecule of potassium chlorate is made up of 1 atom of potassium, 1 atom of chlorine, and 3 atoms of oxygen.

Atoms remain unaltered in all ordinary chemical transformations. During a chemical change molecules of reacting substances first separate into atoms which then combine to form new molecules of the product. Hence:

A chemical change *is one in which the atoms of the reacting molecules are regrouped to form new molecules; a* **physical change** *does not affect a molecule, and hence no new molecules are produced in a physical change.*

Atomic weight.—Every kind of atom, according to Dalton's atomic theory, has a definite and constant weight. The atoms of any one element all have the same weight, but the atoms of different elements have different weights.

As the atoms are exeremely minute, their mass is exceedingly small being of the order of 10^{-24} grams ; the mass of an atom of the lightest element hydrogen is only 1.67×10^{-24} grams ; the mass of an atom of uranium is 3.95×10^{-22} grams only. The smallness of an atom is rather difficult to grasp easily—about 3×10^{19} atoms of hydrogen are contained in 1 c.c. of the gas.

It is, therefore, difficult to find out the actual weight of an atom of an element. But the weight of the atom of the element *relative* to that of a standard atom can be easily found out—this relative weight is stated as the atomic weight of the element.

At one time the weight of the hydrogen atom, the lightest known atom, was chosen as the standard by Dalton and its atomic weight was taken as unity. The atomic weight of an element relative to that of hydrogen as unity, therefore, showed how many times an atom of the element was heavier than the hydrogen atom.

The atomic weight is now-a-days determined in terms of the element oxygen as the standard—the atomic weight of oxygen is arbitrarily taken as 16.0000.

The atomic weight of an element is the weight of an atom of the element relative to the weight of the oxygen atom taken as 16.

The atomic weight of an element is, therefore, the number of times one atom of its is heavier than the sixteenth part of the atom of oxygen. On the oxygen standard the atomic weight of hydrogen is 1.008.

Exercises

1. Do you consider the following to be physical or chemical changes :

   (a) common salt is shaken with water until no further solid remains,
   (b) a magnesium ribbon is heated in air until it takes fire,
   (c) a piece of sodium floats on water, finally disappearing,
   (d) the dissolution of sugar in a cup of tea,
   (e) ammonium chloride, when heated in a test tube, vaporises and condenses as a solid on the cooler part of the tube ? Give reasons.

2. What are the differences between physical and chemical changes ?

In what ways does a mixture of iron filings and sulphur differ from iron sulphide ?

3. A piece of iron rusts on exposure to the air and increases in weight, while a piece of charcoal when ignited, burns away leaving a little ash of negligible weight. How would you reconcile the above facts with the law of conservation of mass ?

Describe an experiment to prove that matter is indestructible.

4. Define (a) element, (b) compound. State if each of the following is an element, a compound, or a mixture ; common salt, water, mercuric oxide, gold, potassium chlorate, air.

What are the chief differences between a compound and a mixture ?

5. What do you understand by the terms *atom*, *atomic weight*, and *molecule* ? The atomic weight of chlorine is 35.5. What does this statement convey to you ? (*P. U. Cal.* 1961)

6. Classify the following changes as purely chemical, purely physical, or as belonging to both : (a) distillation of water, (b) melting of lead, (c) magnetising a knife blade, (d) heating a piece of lime stone, (e) sending electric current through fused common salt, (f) dissolution of copper in nitric acid, (g) electrolysis of water.

7. What is meant by exothermic and endothermic reactions ? Give two examples of each.

III

SYMBOLS, FORMULAE & EQUATIONS

Symbols and formulae.—In order to describe the chemical composition of a substance involving certain ones of the elements a chemist perfers to use, for the sake of convenience, abbreviations for the full name of each element concerned, since they are more quickly written. Thus, the letter H is written for the word hydrogen ; the abbreviation for oxygen is O ; and for nitrogen N. These are referred to as **symbols** of elements. Usually the symbol is the initial letter of the English name for which it stands ; when, however, more than one element has the same initial letter, a pair of letters are necessary ; thus, C stands for carbon ; Cl represents chlorine, and Ca is calcium. Ni is symbol for nickel, and He for helium. Sometimes the symbols are derived from the Latin name of the element. The present system of chemical notation was introduced by the Swedish chemist Berzelius in 1811.

Symbols of a few elements with their Latin names in *italics* are given below :

Antimony (*Stibium*)	Sb	Mercury (*Hydrargyrum*)	Hg
Copper (*Cuprum*)	Cu	Potassium (*Kalium*)	K
Gold (*Aurum*)	Au	Silver (*Argentum*)	Ag
Iron (*Ferrum*)	Fe	Sodium (*Natrium*)	Na
Lead (*Plumbum*)	Pb	Tin (*Stannum*)	Sn

The symbol W for tungsten is derived from the German name wolfram. Symbols of a few more familiar elements are as follows :

Aluminium	Al	Iodine	I
Barium	Ba	Mgnesium	Mg
Boron	B	Manganese	Mn
Bromine	Br	Nitrogen	N
Calcium	Ca	Oxygen	O
Carbon	C	Phosphorus	P
Chlorine	Cl	Platinum	Pt
Chromium	Cr	Silicon	Si
Fluorine	F	Sulphur	S
Hydrogen	H	Zinc	Zn

The symbol of an element does not only stand for the name but also represents *one atom* or *one atomic weight* of the element. Thus O does not stand merely for oxygen ; it represents one atom of oxygen, and also 16 parts by weight of oxygen. The letter N stands for nitrogen. It also means one atom of nitrogen and 14 parts by parts by weight of nitrogen, and so on.

Formulae.—Every substance, be it an element or a compound, has a definite chemical formula—a combination of symbols and numerals written in such a way as to indicate *what kinds of atoms* and *how many of each* are present in *each molecule* of the substance. *A chemical formula symbolically represents the composition of a substance.*

The chemical formula of an element is denoted by its symbol with a numeral placed to its *right* and a little *below* it to show how many of its atoms are contained in a molecule. *The number of atoms* contained in the molecule of an element is known as its **atomicity.** Molecules of common gases oxygen, hydrogen, nitrogen and chlorine, each contain two atoms, i.e., their molecules are *diatomic* and consequently their formulæ are written as O_2, H_2, N_2 and Cl_2. A molecule of phosphorus contains 4 atoms, and hence its formula is P_4. But the inert gases argon, helium, and neon, etc., and most metallic vapours such as mercury and zinc, etc., are *monoatomic*, i.e., their molecules are composed of one atom only, and therefore, their formulæ are A, He, Ne, Hg and Zn, etc.

A molecule of a compound contains a fixed number of atoms of its constituent elements. Its chemical formula is designed by writing down side by side the symbols of its constituent elements, with a numeral to the right and slightly below each symbol in order to show how many atoms of its are contained in the molecule. Thus, a molecule of sulphuric acid contains 2 atoms of hydrogen, 1 atom of sulphur and 4 atoms of oxygen, and hence its formula is written as H_2SO_4—the numeral 1 being always understood. The formula for chalk, also called calcium carbonate, is $CaCO_3$, since it contains 1 atom of calcium, 1 atom of carbon, and 3 atoms of oxygen. Nitre, also known as salt-petre, is denoted by the formula KNO_3. H_2O stands for the formula of water.

The chemical formula of a substance does not merely denote *its composition*, it also represents *one molecule* or *one molecular weight* of it. Thus, water is represented by the formula H_2O ; it means that each molecule of water is composed of 2 atoms of hydrogen and one atom of oxygen, and that its molecular weight is $18(2\times1+16=18)$ parts by weight.

The molecular weight of a substance is the sum of the weights of atoms present in a molecule ; thus, the molecular weight of sulphuric acid, H_2SO_4, which contains 2 atoms of hydrogen, 1 atom of sulphur, and 4 atoms of oxygen, is : $2\times1+1\times32+4\times16=98$.

The formula for oxygen is O_2, and consequently, its molecular weight is 32 $(2\times16=32)$ parts by weight.

The molecular weight of a substance expressed in grams is called the **gram molecule** or sometimes the **gram molecular weight ;** thus 1 gram molecule of sulphuric acid is 98 grams ; one gram molecule of water is 18 grams, and one gram molecule of chalk is 100 grams. and so on.

A number placed to the immediate left of a chemical formula indicates the number of molecules of the substance. $5H_2SO_4$, for example, denotes 5 molecules of sulphuric acid ; $6H_2O$ means 6 molecules of water.

Two atoms of nitrogen are contained in a molecule of nitrogen and its formula is written as N_2 ; 2N, however, means 2 atoms of nitrogen; $5N_2$, stands for 5 molecules of nitrogen which contain 10 atoms of nitrogen ; 10 atoms of nitrogen are expressed as 10N. $7O_2$ stands for 7 molecules of oxygen ; 7O means 7 atoms of oxygen.

Valency.—**Chemical affinity** between substances is a measure of their tendency to undergo a chemical change. Quite commonly dissimilar substances exhibit greater chemical affinity—substances of opposite chemical nature easily enter into a chemical reaction ;

thus a metal generally reacts easily with a non-metal. Again, it is found that the relative affinity of an element is not the same for different elements. Thus, chlorine is said to possess a greater affinity for sodium than for copper, since it reacts more readily and vigorously with sodium than with copper.

Chemical compounds are formed by the union of atoms of different elements in simple numerical proportions. It is, however, found that the combining power of atoms of different elements is not the same. Thus, if one atom of oxygen is considered, it is impossible to make more than 2 atoms of hydrogen combine with it. This holds good for all other elements. There is, therefore, a certain number of atoms of hydrogen with which one atom of an element would combine (if it combines with hydrogen at all). Thus, in the following compounds one atom of the elements combines with 1, 2, 3, or 4 atoms of hydrogen :

Hydrogen chloride HCl	Ammonia	NH_3
Water H_2O	Methane	CH_4

In these instances one atom of each of the elements chlorine, oxygen, nitrogen, and carbon are capable of combining with 1, 2, 3, and 4 atoms of hydrogen respectively, and consequently their **combining capacities,** or what is called **valency,** are 1, 2, 3, and 4 respectively. It is found that in none of the compounds of hydrogen does an atom of hydrogen combine with more than one atom of any element—the only exception in which one atom of hydrogen unites with more than one atom of another element is hydrazoic acid, N_3H; and consequently *an atom of hydrogen has the least combining capacity.* Hydrogen is therefore, taken as the standard of valency, and its valency is taken to be 1. The valency of other elements is compared with that of the standard element.

Valency.—*The valency of an element denotes the combining capacity of its atoms and is measured by the number of hydrogen atoms with which one atom of the element in question would combine.*

The examples cited above, therefore, tell us that chlorine, oxygen, nitrogen, and carbon are *univalent*, *bivalent*, *trivalent*, and *quadrivalent* respectively.

When an element does not directly combine with hydrogen, its valency is determined with reference to other elements of known valency. Thus, aluminium does not combine with hydrogen, but it combines with chlorine, forming the compound aluminium chloride, $AlCl_3$. Hence aluminium is trivalent, since *one atom* of it combines with *three atoms of univalent chlorine.* Oxygen is bivalent, and consequently when it combines with one atom of another element, the latter is also bivalent ; e.g., magnesium is bivalent in magnesium oxide, MgO. The following oxygen compounds are highly illustrative :

Sodium monoxide Na_2O,
Aluminium oxide Al_2O_3,
Phosphorus pentoxide P_2O_5
Chlorine heptoxide Cl_2O_7,

Magnesium oxide MgO,
Silicon dioxide SiO_2,
Sulphur trioxide SO_3,
Osmium tetroxide OsO_4.

The above examples show that sodium, magnesium, aluminium, silicon, phosphorus, sulphur, chlorine, and osmium are univalent, bivalent, trivalent, quadrivalent, pentavalent, hexavalent, heptavalent and octavalent respectively. 8 is the highest valency known.

The inert gases argon, helium neon, etc., form no compounds with any elements, and as such they exhibit no valency. They are elements of zero valency.

Variable valency.—The valency of many elements may vary in different compounds. An element may exhibit more than one valency either (i) in its compounds with the *same* element ; thus iron is bivalent in ferrous chloride, $FeCl_2$, and trivalent in ferric chloride, $FeCl_3$; phosphorus is trivalent in phosphorus trichloride, PCl_3, but pentavalent in phosphorus pentachloride, PCl_5 or (ii) in its compounds with *different* elements ; thus nitrogen is trivalent in ammonia, NH_3, but pentavalent in nitrogen pentoxide, N_2O_5 ; sulphur is divalent in hydrogen sulphide H_2S, and hexavalent in sulphur hexafluoride, SF_6.

The valencies of some common elements are given below :

Element	Symbol	Valency	Element	Symbol	Valency
Aluminium	Al	3	Iron	Fe	2,3
Antimony	Sb	3,5	Lead	Pb	2,4
Arsenic	As	3,5	Magnesium	Mg	2
Barium	Ba	2	Manganese	Mn	2,3,4,6,7
Boron	B	3	Mercury	Hg	1,2
Bromine	Br	1,3,5,7	Nitrogen	N	1,2,3,4,5
Calcium	Ca	2	Oxygen	O	2
Carbon	C	4	Phosphorus	P	3,5
Chlorine	Cl	1,3,5,7	Potassium	K	1
Chromium	Cr	2,3,6	Silicon	Si	4
Copper	Cu	1,2	Silver	Ag	1
Fluorine	F	1	Sodium	Na	1
Gold	Au	1,3	Sulphur	S	2,4,6
Hydrogen	H	1	Tin	Sn	2,4
Iodine	I	1,3,5,7	Zinc	Zn	2

Variable valency of few metals and nomenclature of their compounds with reference to chlorides are noted :

Metal	Valency	Chloride
Cuprous copper	1	Cuprous chloride, CuCl
Cupric copper	2	Cupric chloride, $CuCl_2$
Mercurous mercury	1	Mercurous chloride, Hg_2Cl_2
Mercuric mercury	2	Mercuric chloride, $HgCl_2$
Ferrous iron	2	Ferrous chloride, $FeCl_2$
Ferric iron	3	Ferric chloride $FeCl_3$
Chromous chromium	2	Chromous chloride, $CrCl_2$
Chromic chromium	3	Chromic chloride, $CrCl_3$
Manganous manganese	2	Manganous chloride, $MnCl_2$
Manganic manganese	3	Manganic chloride, $MnCl_3$
Stannous tin	2	Stannous chloride, $SnCl_2$
Stannic tin	4	Stannic chloride, $SnCl_4$
Plumbous lead	2	Plumbous chloride, $PbCl_2$
Plumbic lead	4	Plumbic chloride, $PbCl_4$.

Radicals.—In many compounds a group of atoms of different elements behaves collectively *like a single atom* and takes part *as a whole* in chemical reactions ; such a group of atoms is called a radical (also called *compound radical*). Thus, ammonia reacts with hydrochloric acid producing ammonium chloride, NH_4Cl, where the group NH_4, plays the part of a univalent metal and is called an *ammonium radical*.

The formula for sulphuric acid is H_2SO_4—the sulphate group SO_4, is bivalent since it combines with 2 hydrogen atoms. Similarly, the carbonate group CO_3, is bivalent in the carbonic acid, H_2CO_3; the nitrate group NO_3, is univalent in the nitric acid, HNO_3; the phosphate group PO_4, is trivalent in phosphoric acid, H_3PO_4.

The hydroxyl group OH in bases is a radical; it is univalent: e.g., caustic soda, NaOH.

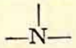
Some common radicals with their valencies are as follows:

Radical	Valency	Radical	Valency
Ammonium NH_4	1	Carbonate CO_3	2
Sulphate SO_4	2	Bicarbonate HCO_3	1
Bisulphate HSO_4	1	Hydroxyl OH	1
Sulphite SO_3	2	Perchlorate ClO_4	1
Bisulphite HSO_3	1	Chlorate ClO_3	1
Nitrate NO_3	1	Chlorite ClO_2	1
Nitrite NO_2	1	Hypochlorite ClO	1
Phosphate PO_4	3	Chromate CrO_4	2
Phosphite PO_3	3	Dichromate Cr_2O_7	2
Borate BO_3	3	Manganate MnO_4	2
Ferrocyanide $Fe(CN)_6$	4	Permanganate MnO_4	1
Ferricyanide $Fe(CN)_6$	3	Thiosulphate S_2O_3	2

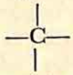
Except ammonium NH_4 which is a univalent positive radical, the rest are negative radicals and play the part of a non-metallic element in a compound.

Structural Formulae.—The formula of a compound may be designed graphically indicating how the atoms are linked in a molecule. For this purpose each atom of an element is assumed to possess one or more hands which are represented by bonds or short straight lines, drawn from the symbol of the atom—the number of lines drawn corresponds to the valency of the element. The valency of hydrogen, oxygen, nitrogen, and carbon, for example, are graphically designed as:

$—H—$ $—O—$



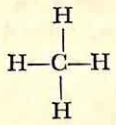
$$—\overset{|}{N}—$$



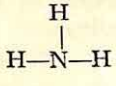
$$—\underset{|}{\overset{|}{C}}—$$

These bonds unite in pairs in chemical combination, i.e., the hand on one atom holds the hand on another; thus the formulas for water H_2O, hydrogen peroxide, H_2O_2, methane, CH_4, and ammonia, NH_3, are represented as:

$H—O—H$ $H—O—O—H$



$$\begin{array}{c} H \\ | \\ H—C—H \\ | \\ H \end{array}$$



$$\begin{array}{c} H \\ | \\ H—N—H \end{array}$$

The sulphate group has 2 valency bonds so that the structural formula for sulphuric acid is:

$$H—SO_4—H$$

A pair of mutually satisfying bonds produce a single bond in a compound, as illustrated in the above compounds. In like manner, two pairs of bonds produce a double bond, and three pairs a triple bond.

A compound is said to be **saturated** when all the valencies of the constituent atoms are *fully satisfied*, and **unsaturated** when the valencies are only *partially* satisfied. Water, hydrogen peroxide, methane and ammonia, all in the above illustrations are

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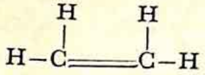
saturated compounds. Ethylene, C_2H_4 and acetylene, C_2H_2, are unsaturated ; they are represented as :



$H-C=C-H$ (with H above each C)

Ethylene

$H-C\equiv C-H$

Acetylene

Ethylene contains a double bond, and acetylene a triple bond. Double and triple bonds in compounds indicate unsaturation in them.

The names of compounds.—Compounds are generally given such names as to indicate their composition. The following examples would clearly indicate the system of *chemical nomenclature*, i.e., naming of substance.

Compounds of two elements are called **binary compounds.** In naming such compounds, the name of the metal (or the more positive element) appears first, followed by the name of the non-metal (or the more negative element) with the termination **-ide.**

An **oxide** is a binary compound of an element with oxygen ; a **chloride** is a compound of an element with chlorine. In like manner the binary compounds in which one of the elements is sulphur, hydrogen, bromine, iodine, nitrogen, etc., are given the names, **sulphide, hydride, bromide, iodide, nitride,** etc., respectively, e.g.

Magnesium oxide MgO
Hydrogen sulphide H_2S
Potassium iodide KI
Magnesium nitride Mg_3N_2
Carbon tetrachloride CCl_4

Aluminium chloride $AlCl_3$
Calcium hydride CaH_2
Sodium bromide $NaBr$
Chlorine monoxide Cl_2O
Calcium carbide CaC_2

In binary compounds when an element combines with another forming more than one compound, the suffix **-ous,** or **-ic** is added to the metal (or less electronegative element) to denote the lower or higher proportion of the element respectively. Examples are :

Ferrous chloride $FeCl_2$
Stannous chloride $SnCl_2$
Mercurous oxide Hg_2O
Cuprous oxide Cu_2O
Nitrous oxide N_2O

Ferric chloride $FeCl_3$
Stannic chloride $SnCl_4$
Mercuric oxide HgO
Cupric oxide CuO
Nitric oxide NO

The prefixes **mono-, di-, tri-,** etc., are sometimes added to the non-metal or to the more negative element denoting the number of its atom in the molecule. In a series of oxides the prefix **per-** is usually, but not always, added to the one containing most oxygen, e.g.

Sodium monoxide Na_2O
Chlorine monoxide Cl_2O
Chlorine heptoxide Cl_2O_7
Phosphorus trioxide P_2O_3
Sulphur dioxide SO_2

Sodium peroxide Na_2O_2
Carbon dioxide CO_2
Chlorine dioxide ClO_2
Phosphorus pentoxide P_2O_5
Sulphur trioxide SO_3

Compounds containing three elements are called **ternary compounds ;** e.g., sulphuric acid, H_2SO_4 ; potassium chlorate, $KClO_3$; calcium carbonate, $CaCO_3$.

How to write a formula.—When an element A reacts with another element B to form a compound, the valency of A must balance that of B such that the valency of the compound as a whole is nil ; consequently valency of A must be equal and opposite to that of B, or in other words :

total valency due to A = total valency due to B

i.e. no. of atoms of A × valency of A = no. of atoms of B × valency of B.

$$\text{or} \quad \frac{\text{number of atoms of A}}{\text{number of atoms of B}}=\frac{\text{valency of B}}{\text{valency of A}}$$

Hence, the elements A and B unite in the *simple inverse ratio of their valencies*. The relation holds equally good when radicals are involved in a chemical change. To arrive at a formula of a compound therefore :

(i) Write the symbols of A and B side by side—the metal or the more positive element or radical to the left and the non-metal or less positive element or radical to the right, and

(ii) Indicate by numerals their valencies at the top ; finally

(iii) Shift the valencies *cross-wise* to the lower right of the opposite-partners.

Example are :

Compound	Symbol with valency	Formula
Aluminium oxide	Al^3O^2	Al_2O_3
Aluminium sulphate	$Al^3SO_4{}^2$	$Al_2(SO_4)_3$
Calcium phosphate	$Ca^2PO_4{}^3$	$Ca_3(PO_4)_2$
Copper nitrate	$Cu^2NO_3{}^1$	$Cu(NO_3)_2$

When the valencies are divisible by a common factor, they are first reduced to a simple ratio and then the method is applied :

Compound	Symbol with valency	Simple ratio	Formula
Aluminium phosphate	$Al^3PO_4{}^3$	$Al^1PO_4{}^1$	$AlPO_4$
Magnesium oxide	Mg^2O^2	Mg^1O^1	MgO
Carbon dioxide	C^4O^2	C^2O^1	CO_2

Bicarbonates contain the univalent radical, HCO_3, as in $NaHCO_3$, $Ca(HCO_3)_2$ and $Fe(HCO_3)_2$, whereas the *bisulphates* contain the univalent radical, HSO_4, as in the compounds $NaHSO_4$ and $KHSO_4$.

Chemical equations.—A chemical change that matter undergoes is called a chemical reaction, and may be represented by equations involving symbols of atoms of the elements and formulæ of molecules. *A chemical equation*, therefore, *represents with the aid of symbols and formulae, a chemical reaction.* In writing a chemical equation the formulæ of the reactants are connected by plus (+) signs, so also the products of the reaction—the set of the reactants being separated from the set of the products by a sign of equality (=). For example, potassium chlorate, when strongly heated, loses oxygen, and is converted into potassium chloride :

Potassium chlorate = potassium chloride + oxygen.

Replacing each name by the formulæ of the substances, the equation becomes : $KClO_3 = KCl + O_2$.

This equation is incomplete, and is said to be *unbalanced*, since 3 atoms of oxygen are contained in $KClO_3$ but only 2 are accounted for among the reaction products. This cannot be remedied by writing O_3 on the right instead of O_2, for this wouid mean writing an incorrect formula for oxygen. By doubling the whole expression we get : $2KClO_3=2KCl+3O_2$, for a balanced equation. The equation reads thus : potassium chlorate *yields* or *produces* (which the sign of equality denotes) potassium chloride *and* (plus is read '*and*') oxygen.

Significance of a chemical equation.—A chemical equation has a *qualitative* as well as *quantitative* significance. It indicates the *nature* and the *relative amounts by weight* (and also *by volumes*, in the case of gases) of different substances involved in a chemical reaction. Let us consider the equation $C+O_2=CO_2$.

It reads in a purely qualitative way as "carbon reacts with oxygen to form carbondioxide. But its quantitative meaning is : "one atom of carbon unites with one molecule of oxygen to yield one molecule of carbondioxide." Also

$$\begin{array}{ccccc} C & + & O_2 & = & CO_2 \\ 12 & & 32 & & 44 \end{array}$$

Expressing the atomic weights and molecular weights in grams, we may interpret the equation thus : *one gram atomic weight* of carbon unites with *one gram molecular weight* of oxygen to produce 1 *gram molecular weight* of carbondioxide. The gram atomic weight of carbon is 12 ; the gram molecular weight of oxygen is 32 and that of carbon dioxide 44. Consequently the full significance of the equation is : 12 grams of carbon unite with 32 grams of oxygen to give 44 grams of carbon dioxide. It will be established later that one gram molecular weight of any gas occupies a volume of 22.4 litres at 0°C and at a pressure of 760 mm. of mercury, i.e., at N.T.P.

$$\begin{array}{ccccc} C & + & O_2 & = & CO_2 \\ 12 & & 22.4 \text{ litres} & & 22.4 \text{ litres} \end{array}$$

The equation may, therefore, also be interpretted as : "12 grams of carbon unite with 22.4 litres of oxygen at N.T.P. to produce 22.4 litres of carbon dioxide at N.T.P."

Balancing a Chemical Equation.—A chemicial equation must satisfy the following points :

(i) It should represent *a chemical change that does actually take place.*

(ii) *It must balance*, i.e., it must obey the law of conservation of mass, and as such the number of atoms of *each element* on either sides of the sign of equality must be same.

(iii) All the substances appearing in an equation should be represented by their *molecules*—representation of elements must also be *molecular* and not atomic, except in the case of monatomic molecules like Na and Hg etc. Usual practice is to represent *elementary gases* by their molecular formulæ, e.g., H_2, O_2, N_2, Cl_2, F_2, etc. *Solid elements* in the uncombined state are denoted by their symbols only, such as the metals Zn, Al, Fe, Sn, Pb, etc., and the non-metals C, Si, B, S, etc.

Formulæ of the following compounds further illustrate the method —the number within bracket denotes the valency.

	Oxide O (2)	Hydroxide OH (1)	Nitrate NO_3 (1)	Chloride Cl (1)	Carbonate CO_3 (2)	Sulphate SO_4 (2)	Phosphate PO_4 (3)
Sodium, Na (1)	Na_2O	NaOH	$NaNO_3$	NaCl	Na_2CO_3	Na_2SO_4	Na_3PO_4
Calcium, Ca (2)	CaO	$Ca(OH)_2$	$Ca(NO_3)_2$	$CaCl_2$	$CaCO_3$	$CaSO_4$	$Ca_3(PO_4)_2$
Aluminium, Al (3)	Al_2O_3	$Al(OH)_3$	$Al(NO_3)_3$	$AlCl_3$	—	$Al_2(SO_4)_3$	$AlPO_4$
Iron, *ic*, Fe (3)	Fe_2O_3	$Fe(OH)_3$	$Fe(NO_3)_3$	$FeCl_3$	—	$Fe_2(SO_4)_3$	$FePO_4$
Iron, *ous*, Fe (2)	FeO	$Fe(OH)_2$	$Fe(NO_3)_2$	$FeCl_2$	$Fe(CO_3)$	$FeSO_4$	$Fe_3(PO_4)_2$
Copper, *ic*, Cu (2)	CuO	$Cu(OH)_2$	$Cu(NO_3)_2$	$CuCl_2$	$CuCO_3$	$CuSO_4$	$Cu_3(PO_4)_2$
Copper, *ous*, Cu (1)	Cu_2O	—	—	CuCl	—	Cu_2SO_4	—
Tin, *ic*, Sn (4)	SnO_2	$Sn(OH)_4$	$Sn(NO_3)_4$	$SnCl_4$	—	$Sn(SO_4)_2$	—
Tin, *ous*, Sn (2)	SnO	$Sn(OH)_2$	$Sn(NO_3)_2$	$SnCl_2$	$SnCO_3$	$SnSO_4$	$Sn_3(PO_4)_2$
Mercury, *ic* (2)	HgO	—	$Hg(NO_3)_2$	$HgCl_2$	$HgCO_3$	$HgSO_4$	$Hg_3(PO_4)_2$
Mercury, *ous* (1)	Hg_2O	—	$Hg_2(NO_3)_2$	Hg_2Cl_2	Hg_2CO_3	Hg_2SO_4	$Hg_3(PO_4)$
Ammonium, NH_4 (1)	—	NH_4OH	NH_4NO_3	NH_4Cl	$(NH_4)_2CO_3$	$(NH_4)_2SO_4$	$(NH_4)_3PO_4$

Illustrations.—For simple reactions such as formation of water from its elements, first :

(i) Write a skeleton equation denoting the compounds by their molecular formulae and the elements by their symbols, as

Hydrogen + oxygen = water

$$H + O = H_2O$$

(ii) Balance the equation such that every atom on the left is found on the right of the equation, hence

$$2H + O = H_2O$$

(iii) Finally, represent every substance by its molecule, thus

$$2H_2 + O_2 = 2H_2O$$

The steps involved in arriving at a balanced chemical equation are illustrated by the following examples :

(i) Iron reacts with oxygen to yield ferric oxide.

Iron + oxygen = ferric oxide

$$Fe + O = Fe_2O_3 \quad \ldots \quad \text{(i)}$$

$$2Fe + 3O = Fe_2O_3 \quad \ldots \quad \text{(ii)}$$

$$4Fe + 3O_2 = 2Fe_2O_3 \quad \ldots \quad \text{(iii)}$$

Equation (iii) is the properly balanced equation.

(ii) Nitrogen combine with red-hot magnsium to produce magnesium nitride.

Magnesium + nitrogen = magnesium nitride

$$Mg + N = Mg_3N_2 \quad \ldots \quad \text{(i)}$$

$$3Mg + 2N = Mg_3N_2 \quad \ldots \quad \text{(ii)}$$

$$3Mg + N_2 = Mg_3N_2 \quad \ldots \quad \text{(iii)}$$

The last equation is the properly balanced one. Magnesium nitride is decomposed by water to yield magnesium hydroxide and ammonia.

Magnesium nitride + water = magnesium hydroxide + ammonia

$$Mg_3N_2 + HOH = Mg(OH)_2 + NH_3 \quad \ldots \quad \text{(i)}$$

$$Mg_3N_2 + 6HOH = 3Mg(OH)_2 + 2NH_3 \quad \ldots \quad \text{(ii)}$$

Equation (ii) is properly balanced—water is written here as HOH for convenience.

(iii) Common salt reacts with hot and strong sulphuric acid to produce sodium sulphate and hydrochloric acid.

Common salt + sulphuric acid = sodium sulphate + hydrochloric acid

$$NaCl + H_2SO_4 = Na_2SO_4 + HCl \quad \ldots \quad \text{(i)}$$

$$2NaCl + H_2SO_4 = Na_2SO_4 + 2HCl \quad \ldots \quad \text{(ii)}$$

(iv) Carbon dioxide turns lime water milky due to the formation of a white precipitate of calcium carbonate and water.

Lime water + carbon dioxide = Calcium carbonate + water

$$Ca(OH)_2 + CO_2 = CaCO_3 + H_2O$$

(v) Chalk dissolves in hydrochloric acid with an effervescence of carbon dioxide :

Chalk + hydrochloric acid = calcium chloride + water + carbon dioxide

$$CaCO_3 + HCl = CaCl_2 + H_2O + CO_2 \quad \ldots \quad \text{(i)}$$

$$CaCO_3 + 2HCl = CaCl_2 + H_2O + CO_2 \quad \ldots \quad \text{(ii)}$$

Equation (ii) is properly balanced.

(vi) Ammonium chloride reacts with slaked lime giving ammonia :

Ammonium chloride + slaked lime = calcium chloride + water + ammonia

$$NH_4Cl + Ca(OH)_2 = CaCl_2 + H_2O + NH_3 \quad \ldots \quad \text{(i)}$$

Balancing, $2NH_4Cl + Ca(OH)_2 = CaCl_2 + 2H_2O + 2NH_3 \quad \ldots \quad \text{(ii)}$

Balancing by Partial Equations.—When it is comparatively difficult to balance a chemical equation by inspection, it is advisable to arrive at the balance deuqation by writing down the equation in steps—the steps representing the possible course of reaction. Each step is represented by a separate *partial equation*, and the partial equations are finally added to get the balanced equation—if and when necessary, the partial equations are multiplied by suitable integers for correctly balancing the final equation. The method is illustrated below :

(i) Hot and concentrated sulphuric acid reacts with copper turnings to produce sulphur dioxide :
Sulphuric acid decomposes into water, sulphur dioxide and oxygen. The oxygen then converts copper into copper oxide which dissolves in the sulphuric acid to give copper sulphate and water.

$$\begin{array}{rcl}
H_2SO_4 & = & H_2O + SO_2 + O \\
Cu + O & = & CuO \\
CuO + H_2SO_4 & = & CuSO_4 + H_2O \\
\hline
Cu + 2H_2SO_4 & = & CuO + 2H_2O + SO_2
\end{array}$$

(ii) Copper reacts with moderately strong nitric acid to yield nitric oxide.

$$\begin{array}{rcl}
2HNO_3 & = & H_2O + 2NO + 3O \\
3Cu + 3O & = & 3CuO \\
3CuO + 6HNO_3 & = & 3Cu(NO_3)_2 + 3H_2O \\
\hline
3Cu + 8HNO_3 & = & 3Cu(NO_3)_2 + 4H_2O + 2NO
\end{array}$$

(iii) Sodium decomposes cold water to yield caustic soda and hydrogen.

$$\begin{array}{rcl}
H_2O + 2Na & = & H_2 + Na_2O \\
Na_2O + H_2O & = & 2NaOH \\
\hline
2Na + 2H_2O & = & 2NaOH + H_2
\end{array}$$

(iv) Hydrogen peroxide reacts with a solution of potassium permanganate acidified with dilute sulphuric acid, evolving oxygen in the cold.

Potassium permanganate decomposes in the acid solution yielding oxygen and forming oxides of potassium and manganese which are neutralised by sulphuric acid to give salt and water. Hydrogen peroxide also breaks up releasing oxygen. The equation may be built up as follows :

$$\begin{array}{rcl}
2KMnO_4 & = & K_2O + 2MnO + 5O \\
K_2O + H_2SO_4 & = & K_2SO_4 + H_2O \\
2MnO + 2H_2SO_4 & = & 2MnSO_4 + 2H_2O \\
5H_2O_2 & = & 5H_2O + 5O \\
5O + 5O & = & 5O_2 \\
\hline
2KMnO_4 + 3H_2SO_4 + 5H_2O_2 & = & K_2SO_4 + 2MnSO_4 + 8H_2O + 5O_2
\end{array}$$

(v) Potassium iodide reacts with hot and concentrated sulphuric acid, evolving violet vapours of iodine :

$$\begin{array}{rcl}
2KI + 2H_2SO_4 & = & 2KHSO_4 + 2HI \\
H_2SO_4 & = & H_2O + SO_2 + O \\
2HI + O & = & H_2O + I_2 \\
\hline
2KI + 3H_2SO_4 & = & 2KHSO_4 + 2H_2O + SO_2 + I_2
\end{array}$$

Exercises

1. What do you understand by the terms *atom, molecule, valency* ?

Write down the formulæ, and calculate the molecular weight of the following compounds ; copper sulphate, calcium bicarbonate, ferric sulphate, ferrous sulphate, sodium bisulphate, ammonium carbonate, stannic chloride, mercurous chloride, aluminium sulphate, ferric hydroxide.

2. Write down the equations for the followring reactions :
   (a) iron is heated in a current of chlorine,
   (b) the action of zinc on copper sulphate solution,
   (c) the burning of phosphorus in air,
   (d) an iron knife blade is dipped into copper sulphate solution,
   (e) the combination of phosphorus and iodine,
   (f) the decomposition of limestone by heat,
   (g) the action of dilute sulphuric acid on iron filings,
   (h) the action of heat on potassium chlorate.

3. Translate the following equations into symbols :
   (i) limestone + hydrochloric acid = calcium chloride + water + carbon dioxide,
   (ii) barium chloride + sodium sulphate = barium sulphate + sodium chloride,
   (iii) sodium chloride + sulphuric acid = sodium bisulphate + hydrochloric acid,
   (iv) silver nitrate + sodium chloride = silver chloride + sodium nitrate,
   (v) sodium + water = caustic soda + hydrogen,
   (vi) sulphuric acid + iron = ferrous sulphate + hydrogen,
   (vii) calcium oxide + water = slaked lime,
   (viii) ferric oxide + aluminium = aluminium oxide + iron,
   (ix) sodium hydroxide + hydrochloric acid = sodium chloride + water.

4. Explain why both sides of a chemical equation must balance. Balance the following equations :

(a) $Fe_2O_3 + CO = Fe + CO_2$; (b) $Ca + H_2O = Ca(OH)_2 + H_2$,
(c) $KClO_3 = KCl + O_2$; (d) $Sn + Cl_2 = SnCl_4$,
(e) $PbS + H_2O_2 = PbSO_4 + H_2O$; (f) $H_2 + O_2 = H_2O$.

5. What informations do the equations : (a) $2H_2 + O_2 = 2H_2O$; (b) $C + O_2 + CO_2$, convey to you ? Balance the following equations :

(i) $Fe + HCl = FeCl_2 +$; (ii) $Ca(OH)_2 + HCl = CaCl_2 +$;
(iii) $P + O_2 =$; (iv) $Pb(NO_3)_2 = PbO + NO_2 +$;
(v) $CuSO_4 + Fe = FeSO_4 +$; (vi) $Al + Cl_2 = AlCl_3$.

What is chemical equation ? On what principles is it formed and what does it convey ?

IV

ACIDS, BASES, AND SALTS

Acid.—It is found that certain properties are shared by all acids ; all acids, for example, have a sour taste—the very name acid comes from a Latin word meaning sour. **Acids turn blue litmus red ;** thus, when a few drops of blue litmus solution are added to a little dilute sulphuric acid in a test tube, the entire solution turns red. Many acids, acting on certain metals, would liberate the hydrogen gas. When a little dilute sulphuric acid, for example, is added to a piece of granulated zinc in a test tube, there is a brisk evolution of hydrogen gas. The gas may be burnt in a jet with a pale blue flame. The above properties are not, however, sufficiently precise to define an acid.

An **acid** *is a compound containing one or more* **replaceable** *hydrogen atoms which may be partially or wholly replaced by a metal forming a salt, when acted upon by certain metals, metallic oxides, and hydroxides.*

Thus, iron reacts with dilute sulphuric acid, producing ferrous sulphate and liberating hydrogen ; ferrous sulphate is the salt of sulphuric acid.

$$Fe + H_2SO_4 = FeSO_4 + H_2$$

Zinc oxide reacts with sulphuric acid producing zinc sulphate (which is a salt of sulphuric acid), and water :

$$ZnO + H_2SO_4 = ZnSO_4 + H_2O$$

Calcium hydroxide dissolves in nitric acid forming calcium nitrate and water ; calcium nitrate is the salt of nitric acid.

$$Ca(OH)_2 + 2HNO_3 = Ca(NO_3)_2 + 2H_2O$$

The acids are divided into two classes : the **hydracids** and the **oxyacids.** The hydracids do not contain oxygen—besides hydrogen they contain another non-metallic element (or radical) only.

They take the affix -ic and the prefix hydro- in their names e.g., hydrofluoric acid, HF ; hydrochloric acid, HCl ; hydrobromic acid, HBr ; hydriodic acid, HI ; hydrocyanic acid, HCN.

The oxyacids contain oxygen—besides containing both hydrogen and oxygen they contain another element (or radical).

The ending **-ic** or **-ous** are used to denote acids containing more or less oxygen respectively, e.g.,

Sulphuric acid H_2SO_4	Sulphurous acid H_2SO_3
Nitric acid HNO_3	Nitrous acid HNO_2
Chloric acid $HClO_3$	Chlorous acid $HClO_2$
Phosphoric acid H_3PO_4	Phosphorous acid H_3PO_3

The oxyacids containing less oxygen than the **-ous** acid, have the affix **-ous** and the prefix **hypo-** in their names. The oxyacids having more oxygen than the **-ic** acid, carry the affix **-ic** and the prefix **per-** in their names, e.g.,

Phosphorous acid H_3PO_3	Hypophosphorous acid H_3PO_2
Chlorous acid $HClO_2$	Hypochlorous acid HClO
Chloric acid $HClO_3$	Perchloric acid $HClO_4$

The common mineral acids are hydrochloric acid, HCl, sulphuric acid H_2SO_4, and nitric acid, HNO_3.

Salts.—The term **salt** is commonly applied to sodium chloride NaCl, also known as common salt. But the term salt in chemistry refers to the products formed by the displacement of **replaceable** hydrogen atoms of acids by metals—**normal salts** are produced by the complete replacement, and **acid** or **bisalts** by **partial** replacement of the replaceable hydrogen atoms. A salt is, therefore, a compound in which the replaceable hydrogen atoms of an acid have been replaced by a metal either partially or wholly. Thus, sodium sulphate Na_2SO_4, is a salt, since it is sulphuric acid H_2SO_4, in which two hydrogen atoms have been replaced by two atoms of sodium. Simliarly, sodium chloride NaCl, is a salt, because it is hydrochloric acid HCl, in which the hydrogen atom has been replaced by sodium. Salts of hydracids end in **-ide.**

Acid	Sodium salt
Hydrochloric acid HCl	Sodium chloride $NaCl$
Hydrobromic acid HBr	Sodium bromide $NaBr$
Hydriodic acid HI	Sodium iodide NaI
Hydrofluoric acid HF	Sodium fluoride NaF
Hydrocyanic acid HCN	Sodium cyanide $NaCN$

The termination **-ite** is affixed to the name of the salt of any **-ous** acid, and **-ate** to the salt of any **-ic** acid.

Acid	Sodium salt
Sulphuric acid H_2SO_4	Sodium sulphate Na_2SO_4
Sulphurous acid H_2SO_3	Sodium sulphite Na_2SO_3
Nitric acid HNO_3	Sodium nitrate $NaNO_3$
Nitrous acid HNO_2	Sodium nitrite $NaNO_2$
Carbonic acid H_2CO_3	Sodium carbonate Na_2CO_3
Phosphoric acid H_3PO_4	Sodium phosphate Na_3PO_4
Hypochlorous acid $HOCl$	Sodium hypochlorite $NaOCl$
Chlorous acid $HClO_2$	Sodium chlorite $NaClO_2$
Chloric acid $HClO_3$	Sodium chlorate $NaClO_3$
Perchloric acid $HClO_4$	Sodium perchlorate $NaClO_4$

Salts may contain metals which exhibit variable valency. In such cases, when the metal shows the lower valency, the metallic portion of the name ends in **-ous,** and when it exhibits higher valency, it takes the affix **-ic,** e.g.

Ferrous sulphate $FeSO_4$	Ferric sulphate $Fe_2(SO_4)_3$
Stannous chloride $SnCl_2$	Stannic chloride $SnCl_4$
Cuprous chloride $CuCl$	Cupric chloride $CuCl_2$

Sodium hydrogen sulphate, $NaHSO_4$, is an acid salt of sulphuric acid ; it still contains replaceable hydrogen, and a solution of it turns blue litmus red. It is also called *sodium bisulphate ;* it contains the univalent bisulphate radical HSO_4.

The formula for *sodium bicarbonate* is $NaHCO_3$; it is an acid salt of carbonic acid H_2CO_3. The bicarbonates contain the bicarbonate radical HCO_3, which is univalent. Calcium bicarbonate has the formula $Ca(HCO_3)_2$.

Bases.—A base is a compound (the oxide or hydroxide of a metal) which reacts with an acid to produce a salt and water only.

$$\text{Base}+\text{acid}=\text{salt}+\text{water}$$

(i) Cupric oxide dissolves in sulphuric acid, producing cupric sulphate and water :

$$CuO + H_2SO_4 = CuSO_4 + H_2O$$

(ii) Sodium hydroxide reacts with sulphuric acid, forming sodium sulphate and water : $2NaOH + H_2SO_4 = Na_2SO_4 + 2H_2O$

The acid salt sodium bisulphate is formed when lesser amount of sodium hydroxide is used : $NaOH + H_2SO_4 = NaHSO_4 + H_2O$

(iii) Aluminium oxide reacts with sulphuric acid producing aluminium sulphate and water : $Al_2O_3 + 3H_2SO_4 = Al_2(SO_4)_3 + 3H_2O$

(iv) Ferric oxide dissolves in hydrochloric acid, forming ferric chloride and water :

$$Fe_2O_3 + 6HCl = 2FeCl_3 + 3H_2O$$

An oxide of a metal, if soluble in water produces a **hydroxide.**

$Na_2O + H_2O = 2NaOH$ (sodium hydroxide)
$K_2O + H_2O = 2KOH$ (potassium hydroxide)
$CaO + H_2O = Ca(OH)_2$ (calcium hydroxide).

The hydroxides of metals are compounds of metals with the hydroxyl group, OH ; the metallic hydroxides are bases.

Soluble hydroxides are called alkalis.—The term **alkali** is, therefore, applied to bases which are soluble in water. In addition to their property of forming salts with acids, the alkalis possess the following properties : (i) *their solutions turn red litmus solution blue ;* (ii) *their solutions have a soapy feel when rubbed between the fingers.*

Such substances as sodium hydroxide (also called *caustic soda*), potassium hydroxide (also called *caustic potash*), and calcium hydroxide which are soluble in water, are called alkalis. A solution of calcium hydroxide is known as *lime water.*

Insoluble hydroxides, such as aluminium hydroxide $Al(OH)_3$ and ferric hydroxide $Fe(OH)_3$, are not alkalis, but they are bases ; consequently, *all bases are not alkalis, but all alkalis are bases.*

Ammonia NH_3 dissolves in water producing ammonium hydroxide which is alkaline : $NH_3+H_2O=NH_4OH$ (ammonium hydroxide).

Exercises

1. Write down the names and formulæ of the sodium salts of the following acids : nitrous, hypophosphorous, perchloric, hypochlorous, carbonic, sulphurous, hydriodic, and sulphuric. Name three most important mineral acids.

2. What is meant by a base ? Is there any difference between a base and an alkali ? Is sodium carbonate a base ?

Explain what happens when :

(*a*) water is slowly added to a lump of quick lime,
(*b*) dilute sulphuric acid acts on granules of zinc,
(*c*) concentrated hydrochloric acid acts on ferric oxide,
(*d*) caustic soda solution is slowly added to some hydrochloric acid which has been coloured red with litmus solution,
(*e*) strong hydrochloric acid acts on tin,
(*f*) dilute hydrochloric acid acts on sodium carbonate.

3. Define the terms *acid, base,* and *salt.* What are the properties of an acid ? What information does this equation—

$$NaOH + HCl = NaCl + H_2O$$

convey to you ?

V

COMMON LABORATORY PROCESSES

Matter consisting of one substance only is said to be *pure*. Thus, water is a pure substance, since it contains nothing but water. A sample of muddy water, on the other hand, is impure, since it contains other things besides water. In order to study the properties of a substance it must be obtained in the pure state. A specimen of a pure substance is simply a collection of identical molecules.

Solution.—When a little common salt is shaken in a test tube with water, it seems to disappear, giving a **homogeneous** i.e., a uniform mixture. No trace of the salt can be found, when the liquid is examined under the most powerful microscope. The common salt is said to be dissolved in the water, and a **solution** has been formed. When, however, the common salt is added in successive small amounts to water, and the mixture is stirred, the salt dissolves *up to a certain point* only, forming a uniform mixture ; after this the salt no longer passes into solution, but settles down unchanged. There is thus a limit to the amount of salt that may be dissolved by a given quantity of water at a particular temperature. The composition of a solution is, however, *variable*, because the quantity of salt that dissolves in a given amount of water may vary. *The composition of a solution may vary within certain limits but that of a compound is fixed and definite and can not vary.*

A **solution** *is a homogeneous mixture of two or more substances which has the same composition and physical properties in every part*, the composition of the mixture being, however, capable of variation within certain limits. The different substances are uniformly and intimately mixed with each other in a solution.

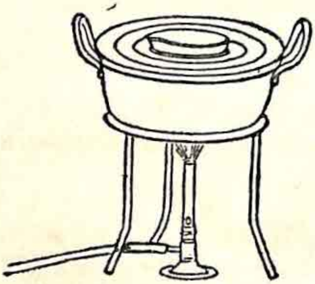


FIG. 9

The common salt that has dissolved in the water, still exists as salt and may be easily recovered by driving off the water by boiling the solution in an *evaporating dish* or a *basin*, usually made of porcelain. When all the water is driven off as steam, a white deposit of common salt is left in the dish ; a deposit such as this, is called a residue. The solution is said to have been evaporated to dryness, and the process is known as **evaporation.** The solution is evaporated on a *water-bath* (fig. 9) to avoid any loss by spirting.

It is obvious that a solution must consist of at least two substances —the substance which has dissolved and that which dissolved it. The dissolved substance is called the **solute,** and the dissolving medium is called the **solvent.** It may, therefore, be written :

solution = solute + solvent.

The solute distributes itself uniformly throughout the solvent without having any tendency to settle on standing. A solution is said to be **dilute** or **concentrated** according as the amount of solute is relatively small or large. Sometimes the terms *weak* or *strong* are used in a similar sense.

A much more precise meaning is conveyed by what is called **concentration** of the solution, which is generally expressed as the number of grams of dissolved substance per 100 grams of the solvent.

Quite commonly when one substance dissolves into another, it is a convention to designate as the *solvent* that component which is present in larger proportion, and to name the other component the *solute*. But this designation is rather arbitrary, particularly when two liquids are miscible in all proportions.

Water is a very common solvent. Many substances like rubber, oil, grease, wax, tar, etc., are not soluble in water. Tar, oil and grease are, however, readily soluble in petrol, and hence the use of petrol in the dry cleaning of dirty clothes. Varnish is a solution of shellac in methylated spirit. Alcoholic solutions of medicines are called **tinctures** or **spirits,** e.g., tincture of iodine.

When a solution is referred, it is not necessarily a solution of a solid in a liquid. Gases may dissolve in liquids ; carbon dioxide, for example, is appreciably soluble in water—'aerated waters' such as lemonades and soda waters are but aqueous solutions of carbondioxide under pressure. Some liquids will dissolve each other. Alcohol dissolves in water in all proportions. Gases always dissolve each other in all proportions. The air is a gaseous solution of nitrogen and oxygen mainly. Many solids dissolve some other solids producing a homogenous mixture of solids, referred to as solid solutions. Thus, when gold is melted and some silver is added, the silver dissolves in the gold, and on cooling, a solid solution is produced. Solids may also dissolve gases ; palladium dissolves hydrogen forming a solid solution.

There are many substances which do not dissolve in water ; they are said to be insoluble. Thus, chalk, glass, stone, most metals, sand, cotton, paper, etc., are but few of the insoluble substances.

Filtration.—When a mixture of some sand and common salt is shaken with water, the salt goes into solution while the sand particles remain in suspension. On standing, however, the sand, being heavier, slowly settles down to the bottom, finally leaving a clear liquid at the top, sometimes called the supernatant liquid. The settled solid is known as the **sediment,** and this process of settling down of heavy solids is referred to as **sedimentation.**

The clear supernatant liquid at the top may be carefully poured off without disturbing the settled solids at the bottom. This process of pouring off the supernatant liquid without disturbing the sediment is known as **decantation.**

When a sample of turbid muddy water is allowed to stand undisturbed for some time, the suspended particles of sand and clay, etc., slowly settle and sink to the bottom, and consequently the turbidity clears.

But like such materials as sand and clay, there are many insoluble solids which do not settle quickly. Their separation is effected by filtration.

Filtration *is a process in which a liquid is separated from insoluble solids by pouring the mixture (of liquid and insoluble substance) into some porous material, such as filter paper, cloth, etc., which allows the liquid to pass through but retains the suspended solid particles.*

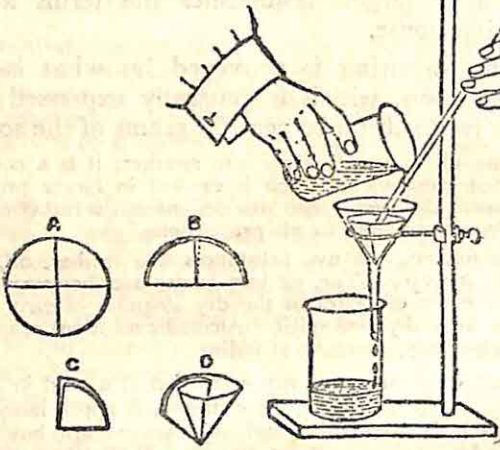


FIG. 10

In the laboratory a special blotting paper, known as filter paper, is usually employed as the porous medium. A circular piece of filter paper is folded into quarters, and then opened out with three quarters on one side and one on the other (fig. 10). It is then fitted in a glass funnel, which may be held in a filter stand. On pouring the mixture of liquid and insoluble solid into the filter paper, the liquid passes through the pores of the paper and is collected in a beaker below—the suspended solid particles are too large to pass through the pores and are held back.

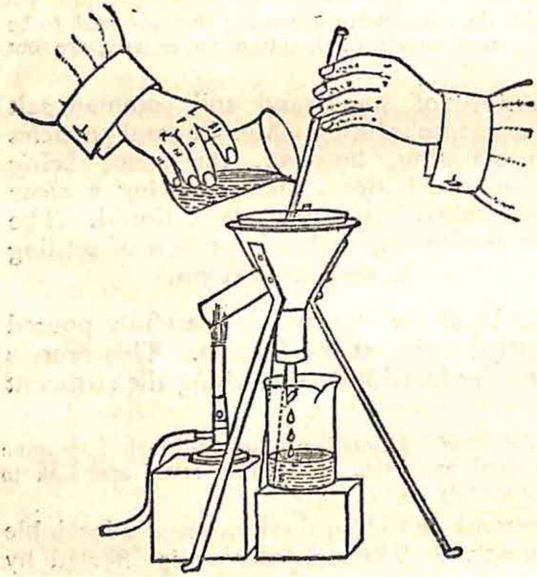


FIG. 11

The liquid passing through the filter paper is called the **filtrate** and the solid retained on the filter paper is called the **residue.** Hot solutions filter more rapidly than cold ones. Figure 11 is a hot filter. Filtration under reduced pressure is a much quicker process.

To separate a mixture of chalk and common salt.—Chalk, also called calcium carbonate, is insoluble in water ; salt dissolves. Some of the mixture is stirred with water, using a glass rod, in a beaker, and poured in thin stream into the filter paper fitted in a glass funnel and moistened with water—care being taken that none comes over the top of the paper. The filtrate is collected in an evaporating dish, and evaporated over a wire gauge on a tripod stand. The common salt is left as a residue after evaporation.

The chalk is retained on the filter paper. Several portions of water are poured over the chalk to wash it free from any adhering salt solution. The filter paper in the funnel is then dried, and the residue of chalk is separated from the filter paper.

Sand (insoluble in water) and common salt can be separated in the same way from their mixture.

To separate gun powder into its constituents.—Gunpowder is an intimate mixture of about 6 parts of potassium nitrate, one part sulphur, and one part charcoal. Of these, only potassium nitrate, also called *nitre* or *saltpetre*, is soluble in water. Sulphur dissolves in carbon disulphide, but charcoal is insoluble in this reagent.

To obtain all three constituents from a given sample of gun powder, some of it is shaken with sufficient quantity of carbon disulphide to dissolve out all the sulphur, and filtered. The filtrate is collected in an evaporating dish, and allowed to evaporate **by itself.** Lemon-yellow crystals of sulphur will deposit in the dish. Carbon disulphide being *very inflammable*, should be kept away from flames.

The residue of nitre and charcoal is held back on the filter paper : this is dried to remove any adhering carbon disulphide. The residue is then separated from the filter paper and stirred with sufficient **hot** water to dissolve out the nitre and filtered.

The filtrate is collected in a basin, and evaporated to dryness, when the potassium nitrate is obtained as a colourless residue. The charcoal is left as a black residue on the filter paper ; it is washed with water to free from nitre solution, dried in a steam oven and separated from the filter paper.

GUNPOWDER

A mixture of nitre, charcoal and sulphur. Add carbon disulphide ; shake ; filter.

Residue
Nitre and charcoal ; dry ; treat with boiling water ; filter.

Filtrate
Solution of sulphur ; evaporate ; residue yellow crystals of sulphur.

Residue
Charcoal ; wash with water ; dry in a steam oven.

Filtrate
Solution of nitre ; evaporate ; colourless residue of nitre.

Asbestos, sand, cotton, glasswool, etc., are often used as filtering medium.

Solution of solids in liquids.—The most important solutions are formed by dissolving solids in liquids. As already mentioned, there is a limit to the amount of solute that may dissolve in a given quantity of water at a particular temperature. When, for example, sugar is added gradually in successive small amounts to water, and stirred, it dissolves in water up to a certain extent only ; after this, the sugar no longer passes into solution but simply settles out unchanged. The solution is then said to be **saturated** with sugar at the temperature of the experiment.

A solution is said to be saturated at a given temperature when it can exist unchanged in contact with the excess of the undissolved solute.

A saturated solution, therefore, contains the maximum amount of a solute in the dissolved state at a given temperature ; if the solution contains less, it is said to be **unsaturated.** An unsaturated solution, therefore, dissolves more of the solute when brought in contact with it.

A solution is said to be **super-saturated,** i.e., **more than saturated,** when it somehow holds more solute than what should be present in its saturated solution at a given temperature.

Sometimes it happens that when a *hot* saturated solution is *cooled* in absence of any dust or undissolved solute, the excess of the solute (i.e., the amount of substance which can no longer be held in solution at the lower temperature) is not thrown out of the solution ; the solution is then said to be *super-saturated.* Such super-saturated solutions are very unstable. Stirring and scratching the wall of the container or the presence of a little dust throws the excess solute out of the solution. An infallible method of making a super-saturated solution throw the excess solute is to drop in a small crystal of the solute into the solution ; the added crystal provides a centre about which the excess solute separates.

To make a super-saturated solution of hypo.—A super-saturated solution of sodium thiosulphate, $Na_2S_2O_3.5H_2O$ also called hypo, is very easily obtained by simply heating the solid substance. Hypo contains combined water known as its water of crystallisation, and when heated it dissolves in this water.

A large test tube is half filled with crystals of 'hypo', and its neck plugged with cotton wool to prevent the entrance of dust. The tube is then heated in a beaker of boiling water. The hypo melts in its own water of crystallisation and forms a super-saturated solution. When this solution is carefully cooled, this remains liquid, and no hypo is deposited—and this is in spite of the fact that initially the entire amount of hypo was present as dry crystals. On removing the plug and putting into the liquid a small crystal of hypo, the liquid at once begins to solidify.

Liquid honey is a super-saturated solution of sugar mainly ; on long standing the sugar will crystallise.

Solubility.—Solubility depends much upon the chemical nature of the solute and of the solvent. Common salt, for example, is soluble in water, but not in alcohol ; while in the same solvent water, hypo is much more soluble than the common salt. Substances differ greatly in the extent to which they dissolve in water.

FIG. 12

Increasing the surface area of solid by powdering hastens its solution greatly. An *agate mortar and pestle* (fig. 12) is generally used to powder a solid in the laboratory.

The solubility of a solid generally increases with the increase of temperature. The solubility of different solutes may not increase to the same extent with the rise in temperature ; the solubility of nitre, for example, increases much more rapidly with temperature than that of the common salt.

The solubility of some substances, such as sodium sulphate, first increases and then decreases with temperature. For every temperature there is a maximum saturation solubility. It is, therefore, convenient to have some standard to compare the extent of solubilities of different substances in solvents.

The **solubility** *of a substance is that weight of it in grams which will saturate* 100 *grams of the solvent at a given temperature.*

Let x gm. of a solute saturate y gm. of a solvent at t°C, then its solubility at $t°\mathrm{C}=100\ x/y$.

If m gms. of solute be present in w gms. of its saturated solution at t°C, then its solubility at $t°C=100\ m/(w\text{-}m)$.

When it is mentioned that the solubility of common salt in water is 36.0 at 20°C, it means that 100 gm. (or 100 c.c., since 1 c.c. of water weighs, very nearly, 1 gm.) of water will just dissolve 36.0 gm. of common salt at 20°C to yield a saturation at the said temperature.

Determination of solubility of nitre.—Suppose it is required to determine the solubility of potassium nitrate, also called nitre, in water at the temperature of the room, i.e., it is required to find the weight of potassium nitrate which will just saturate 100 gm. of water at the temperature of the laboratory.

For this, a saturated solution of potassium nitrate is first prepared by stirring some powdered potassium nitrate with water in a test tube at the room temperature, so that some excess solid is left over at the bottom of the tube—a fact that ensures that the solution is saturated.

The saturated solution is then filtered into an evaporating dish or basin, which has been weighed previously. The whole is then weighed again. The contents of the dish are then carefully evaporated to dryness over a small flame or on a water-bath—care must be taken to avoid loss of salt by spirting, and to ensure that the residue is perfectly dry at the end of heating. The dish with the dry salt is then cooled in a desiccator and weighed again.

Let Weight of dish	a gm.
Weight of dish + nitre solution	b gm.
Weight of dish + nitre	c gm.
∴ weight of nitre	(c−a) gm.
∴ weight of water	(b−c) gm.

i.e., (b−c) gm. of water dissolves (c−a) gm. of nitre

∴ 100 gm. of water dissolve $\frac{(c-a)}{(b-c)}\times 100$ gm. of nitre, which is, therefore, the solubility of nitre.

Solubility of common salt can be similarly determined.

The experiment may be repeated to determine the solubility at different temperatures, using a *thermostat,* which is an arrangement to obtain constant temperatures. The following results for potassium nitrate and sodium sulphate (Glauber's salt) are illustrative.

Temperature	0°	10°	20°	40°	60°	80°	110°
Potassium nitrate	13.3	20.9	32	64	110	169	246
Glauber's salt	5.0	9.0	19.4	49	45	44	42

The solubilities in grams per 100 gm. of water, are plotted against the temperatures. (fig. 13).

Solubility curves.—The dependence of solubility on temperature is represented graphically by means of **solubility curves,** in which the abscissae represent the temperatures, and the ordinates the solubilities. The figure 13 gives the solubility curves of some salts in water. It is seen that the solubility curves of different salts are different in type. The solubility of some salts, e.g., potassium nitrate, increases rapidly with temperature, and hence their curves slope upwards. The curve for common salt is very nearly horizontal, showing that it is hardly more soluble in hot water than in cold. Some salts, such as sodium sulphate, become less soluble at high temperatures. The solubility curves, therefore, give directly the solubility of a substance at a given temperature, and also help us to make a comparative idea of the solubilities of different substances.

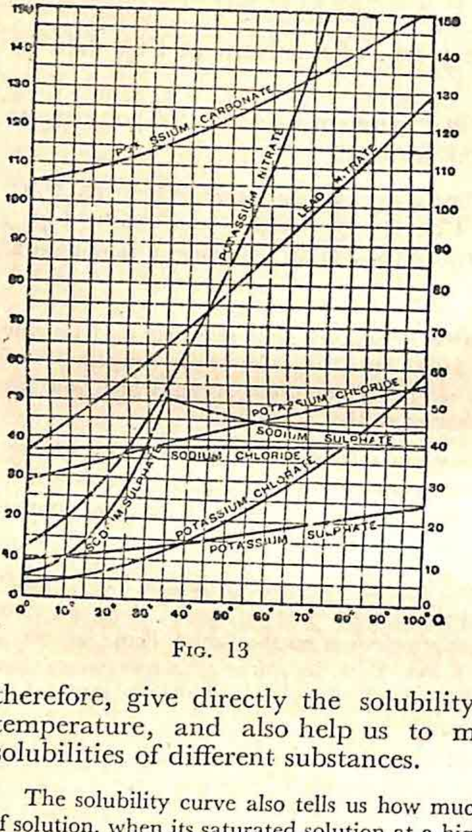


FIG. 13

The solubility curve also tells us how much of the substance will be thrown out of solution, when its saturated solution at a higher temperature is cooled to any lower temperature. Thus the solubility curve tells us that the solubility of nitre is 110 at 60°C, and that at 20°C is 32, and consequently when a saturated solution containing 100 gm. of water is cooled from 60° to 20°, the amount of nitre deposited will be 110 − 32 = 78 gm.

The curves also give information as to which will deposit first when a mixed solution is subjected to evaporation. Thus, when a solution containing potassium chloride and potassium chlorate in equal proportions, is being evaporated at 50°C, the curves tell us that the solution gets saturated with potassium chlorate first as its solubility is less than that of potassium chloride. Hence the potassium chlorate will be deposited first, and until the solution also gets saturated with potassium chloride.

Solutions of gases in liquids.—Liquids can dissolve gases. Carbon dioxide is fairly soluble in water. Air is slightly soluble in water—the dissolved air supports the life of aquatic animals.

Some tap water is taken in a large beaker, and a test tube full of water is inverted over the stem of a funnel placed in the beaker, as shown in the figure 14. The beaker is placed on a wire gauze over a tripod stand; on heating bubbles of gas are collected in the test tube; such water therefore contains dissolved gas. The dissolved gas in ordinary water is mainly air.

Unlike solids the solubility of a gas in liquids decreases with rise in temperature. The solubility of gas, however, increases with pressure. Soda-water is a solution of carbon dioxide in water under pressure; when a soda-water bottle is opened the dissolved gas escapes in bubbles as *effervescence* owing to the reduction of pressure.

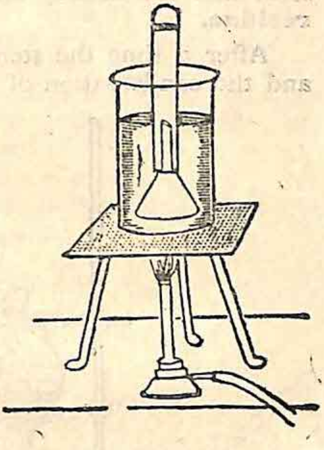


FIG. 14

Solution of liquids in liquids.—Alcohol dissolves in water in all proportions, i.e., is completely miscible. But there are liquids such as water and mercury, which are completely immiscible. Some liquids are partially miscible. Thus, when ether is gradually added to water, it at first dissolves but up to a small extent only; after which two distinct layers separate—the top layer is ether with a trace of water dissolved in it, while the bottom layer is mainly water containing, however, a little dissolved ether. The two layers can be separated by a separating funnel (fig. 15).

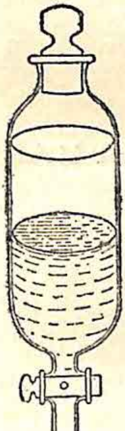


FIG. 15

When the two layers of ether and water are shaken with a little iodine in a separating funnel, it is found that the iodine is shared between the two liquids, but most of it is dissolved out by the ether, as is evident from the darker brown colour of the ether layer. Ether may, therefore, be used to extract iodine from its solution in water. Carbon disulphide also extracts iodine—the solution in this case assumes a beautiful violet colour; the carbon disulphide forms the bottom layer, as it is heavier than water.

The method is widely used for extracting many substances from their solutions in water.

Distillation.—When an aqueous solution is evaporated it is found that the water escapes as steam; the steam may be condensed back into water by cooling.

Distillation is the process of converting a liquid into its vapour by boiling, and then condensing the vapour back to the liquid state by the application of cold.

The process is useful in separating a liquid from a non-volatile solid in solution or suspension.

A sample of muddy water may be purified by distillation. The water is poured into the retort through an opening at the top, called the tubulure. The retort is then set on a wire gauze on a tripod stand, clamped in position and carefully heated by a Bunsen burner (fig. 16). The water boils, giving off steam which is condensed back to water in the receiver placed at the end of the stem of the retort; this is pure water and is called the **distilled water.** The water collecting in the receiver is called the **distillate.** The dissolved solid and the muddy suspensions remain behind in the retort as a **residue.**

After a time the stem of the retort and the receiver get warm, and the condensation of steam is not efficient. Hence, when larger quantities of liquid are to be distilled it is convenient to use a **Liebig's condenser.**

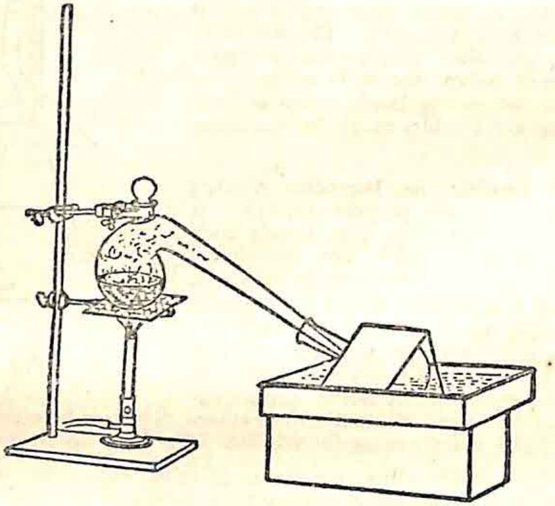


FIG. 16

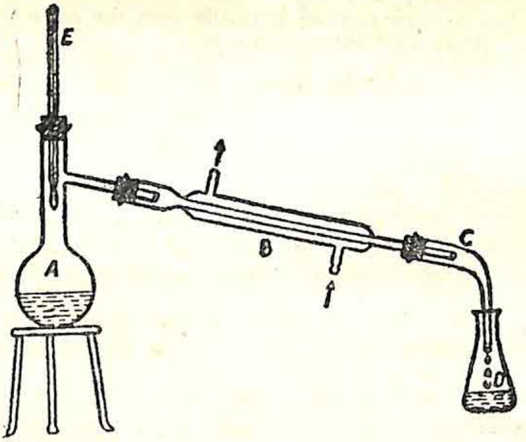


FIG. 17

The muddy water for distillation is taken in a flask (called a distilling flask) with a side tube fused on to the neck. The side tube is connected by means of a cork with the inner glass tube of a Liebig's condenser, itself surrounded by a wider jacket through which a constant stream of cold water is passed—the cooling water is passed in at the bottom, and out at the top of the condenser (fig. 17). The mouth of the flask is closed with a cork—a thermometer may be inserted in the vapour coming from the liquid. The flask is set up on a wire gauze on a tripod stand, clamped in position. On heating the flask, the liquid boils, and the vapour, while passing through the cold inner tube of the condenser, condenses back to the liquid state and collects in the receiver placed at the end of the condenser tube—the liquid collecting is the distillate, the dissolved solid left behind in the flask is the residue.

When stirred with water potassium permanganate gives a pink solution. The coloured solution on distillation, produces a colourless distillate of pure water ; the potassium permanganate remains behind in the flask.

Distilled water is taken in a wash bottle (fig. 18) for common laboratory use.

Fractional distillation—The process of distillation is useful to separate not only *solutions of solids in liquids*, but also solutions of liquids in liquids, sometimes partially only.

When a solution of two volatile liquids with boiling points fairly apart, say, benzene and toluene with boiling points 80° and 110°C respectively, is heated in a distilling flask, each of the liquids gives off its vapour—the vapours formed will, however, contain a greater proportion of the *more volatile benzene* and a smaller proportion of the *less volatile toluene* than the original solution. The vapours on condensation give the distillate ; consequently the distillate is richer in benzene, and the liquid that remains behind in the flask is richer in toluene. This first distillate on second distillation, gives a second distillate which is still richer in benzene—the process may be repeated to finally yield a distillate which is pure benzene.

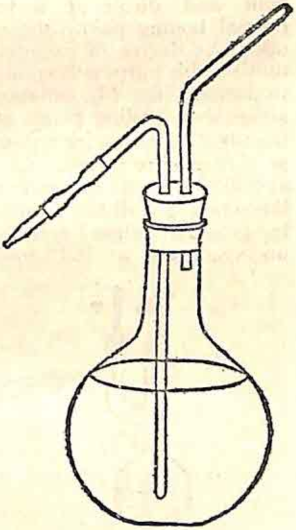


FIG. 18

The residual liquid in the flask after the first distillation, when put to distillation again, leaves a residue still richer in toluene—repeated distillation of the residual liquid, therefore, yields pure toluene as the residue. By repeated distillation, therefore, benzene and toluene can be completely separated. To improve the separation a **fractionating column** (fig. 19) is usually employed.

The fractionating column is inserted between the distilling flask and the condenser.

Such a process of separation of volatile liquids by repeated distillation is known as fractional distillation.

Sometimes the separation is partial only ; thus when a *dilute* solution of hydrochloric acid is fractionally distilled, it is possible to separate pure water on the one hand, and a mixture of hydrochloric acid and water containing 20.2 per cent hydrochloric acid by weight, on the other.

A *dilute* solution of alcohol on fractional distillation, yields pure water, and a mixture of alcohol and water containing 95.57 per cent alcohol by weight.

Vacuum Distillation.—The vapour pressure of a liquid increases or decreases as the temperature rises or falls. A liquid boils when its vapour pressure becomes equal to the superincumbent pressure of air on its surface. The boiling point of a liquid, therefore, rises or falls according as the super-incumbent pressure is increased or decreased. Hence when the pressure on the surface of a liquid is reduced by creating a partial vacuum inside the distilling flask, the liquid boils and distils at a temperature less than its normal boiling point—the extent of lowering depends upon the degree of vacuum created. The distillation unit for this purpose is connected through a manometer to a pump (fig. 20). Substances which decompose near about their boiling points at atmospheric pressure are usually distilled under reduced pressure. This is known as *distillation in vacuum*. Glycerine, for example, boils at 290°C with decomposition at atmospheric pressure, but when it is distilled under reduced pressure,its boiling point is reduced and the decomposition avoided ; glycerine, for example, distils undecomposed at 180° under 12 mm. pressure. For a similar reason hydrogen peroxide is concentrated by distillation in vacuum. It may be safely distilled under reduced pressure—the boiling point at 68 mm. pressure is 84°, and at 26 mm. is 69° ; but it decomposes exclusively into water and oxygen at 151°, which is its boiling point at 760 mm. estimated by extrapolation.

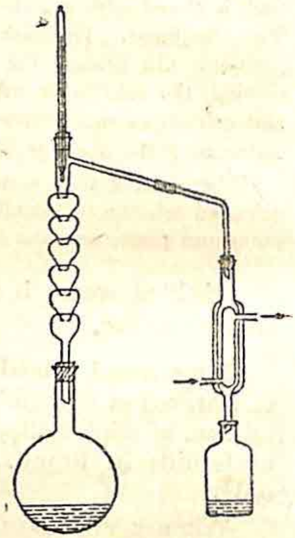
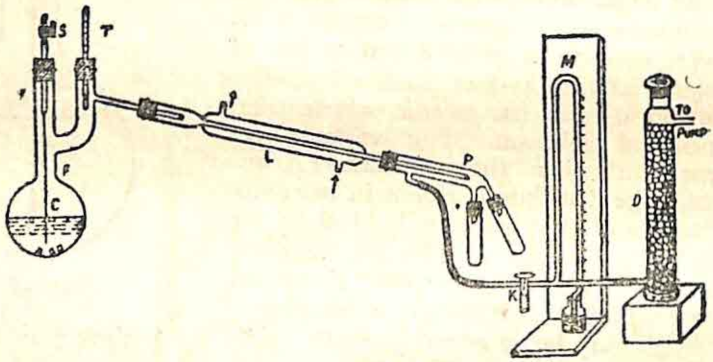


Fig. 19



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Destructive distillation.—When coal is heated out of contact with the air in a closed vessel, it decomposes into several volatile and non-volatile products, thus a gas is given off, called coal gas, a tar is driven off, and an ammonical liquor collects ; the non-volatile products are the coke and the gas carbon.

Such a process of heating a substance like coal out of contact with the air, *when it decomposes into volatile and non-volatile products, is known as destructive distillation, also called dry distillation.*

The dry distillation of coal may be demonstrated in a very simple way. A hard glass test-tube is fitted with a cork and a delivery tube, as shown in the fig. 21, the end of the delivery tube leads into a test-tube which acts as a receiver. Some coal chips are put in the hard glass tube, and then heated fairly strongly : a brown coal tar collects below an aqueous liquor in the receiver test-tube ; a gas issues out through the exit tube, which may be burnt with a sooty flame. The solid residue left in the hard glass tube is the coke.

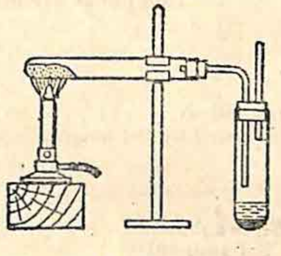


FIG. 21

Sublimation.—It is common experience that most solids when heated long enough, first melt into a liquid which then vaporises. But there are certain volatile solids such as ammonium chloride, iodine, camphor, etc., which when heated pass *directly* into the vapour state without ever becoming a liquid—the vapour condensing into the *same* solid on cooling. The condensed solid is called the **sublimate** and the process **sublimation.** The sublimate has the same composition as the original substance. Thus when some ammonium chloride, also called *sal-ammoniac*, is heated in a dry test tube, the substance disappears from the bottom of the tube and reappears as a white deposit on the cool sides at the upper end of the tube ; ammonium chloride is said to sublime, and the white deposit is the sublimate. The peculiar thing to notice is that ammonium chloride *does not melt*, but turns into vapour without *ever becoming a liquid*, and the vapour condenses to the solid *directly*.

The process of sublimation is sometimes used in the purification of substances. Iodine, for example, is purified by sublimation. Volatile and non-volatile solids may be separated by sublimation.

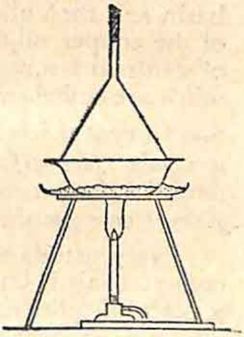
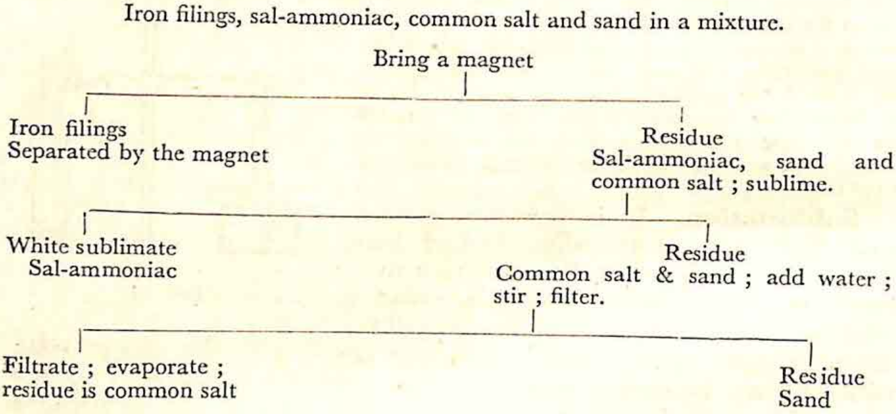


FIG. 22

To separate a mixture of ammonium chloride and sodium chloride.—Some of the mixture is put in a porcelain basin, and covered with an inverted funnel—the end of the stem of the funnel being closed with a paper plug. The basin is then slowly heated over a wire gauze (fig. 22). The ammonium chloride volatilises and collects as a white sublimate on the inner wall of the funnel. When no further sublimation occurs, the flame is removed and the sublimate of ammonium chloride is scraped off on to a filter paper. The non-volatile sodium chloride remains behind in the basin.

To separate a mixture of sand, common salt, iron filings, and sal-ammoniac.—Some of the mixture is spread on a sheet of paper, and the iron filings are completely removed by bringing a magnet several times over it—the iron filings alone are attracted by the magnet. The rest of the mixture, after the removal of iron filings, is put into a basin and covered with a funnel the stem of which is covered with a paper plug. On heating, the sal-ammoniac alone sublimes and deposits on the inner wall of the funnel. When no further sublimation occurs, the basin is allowed to cool ; the funnel is removed and the sal-ammoniac scraped off. The residue of common salt and sand in the basin is shaken with sufficient quantity of warm water to completely dissolve out the salt, and filtered—the sand is the residue; this is dried and separated from the filter paper. The filtrate on evaporation gives the common salt.


Iron filings, sal-ammoniac, common salt and sand in a mixture.
Bring a magnet
Iron filings
Separated by the magnet
Residue
Sal-ammoniac, sand and common salt ; sublime.
White sublimate
Sal-ammoniac
Residue
Common salt & sand ; add water ; stir ; filter.
Filtrate ; evaporate ; residue is common salt
Residue
Sand

Crystallisation.—A cold saturated solution of copper sulphate is prepared by stirring the powdered salt with water, so that an excess of solid is present ; the saturated solution is then warmed until all the solid remaining over has completely dissolved—a few drops of dilute sulphuric acid is added to the solution to prevent the decomposition of the sulphate. The hot solution is poured into a basin and then allowed to cool slowly, when it is found that a portion of the copper sulphate deposits by itself from the solution in the form of solids with a regular and definite geometrical shape ; such deposited solids are called **crystals** and the process is known as **crystallisation.**

A **crystal** *is a homogeneous solid body bounded by plane faces, and having a regular and definite geometrical form, spontaneously assumed during its formation from a solution or from gaseous or liquid state. The geometrical form is an expression of the internal arrangement of the atoms.*

Every solid substance has its crystalline form. A crystal of common salt is cubic, while alum forms octahedral crystals. Usually a piece of solid substance consists of a large number of small crystals which have stuck together.

Crystalline and amorphous solids.—Solids are classified as *crystalline* or *amorphous.* Many substances, such as alum, common salt, sulphur, and ice, separate in the form of crystals when deposited in the solid state from a solution or from a homogeneous melt. Crystals, as already stated, have a *characteristic geometrical form*—crystals are bounded by plane faces which cut one another at definite angles. The atoms are arranged in a definite order, constantly repeated, in a crystalline solid.

Amorphous solids, as their name implies, have no definite crystalline form. Pitch and glass are typical examples of amorphous solids.

When a pure crystalline solid is heated there is a sharp change from the solid to the liquid state at a definite temperature, called the *melting point. A crystalline solid has a definite melting point.*

The melting point of a pure solid is remarkably constant—the melting point of ice, for example, is used to fix the zero of a Centigrade thermometer. When an amorphous solid is heated it does not melt sharply at a definite temperature, but it gradually softens, becomes mobile, and eventually acquires the properties of a liquid ; amorphous solids can, therefore, be regarded as super-cooled liquids.

The preparation of crystals.—Crystals may be prepared : (i) *by concentrating a dilute solution, usually by heat, and then cooling.* When a hot saturated solution of a substance, say potassium dichromate, is cooled slowly, the substance deposits in the form of orange-red crystals. In order to obtain crystals from a dilute solution the solution is taken in a basin and heated on a wire gauze until a drop of the liquid removed on the end of a glass rod begins to crystallise, indicating that the solution is saturated at a lower temperature. The substance then crystallises on cooling. Large crystals are not formed on rapid cooling. Slow and uniform cooling only gives large crystals ; this can be very easily attained in the laboratory by wrapping the evaporating dish with dusters or by covering it with a sheet of paper to prevent contamination with dust.

Seeding with a crystal of the solid in question often breaks super-saturation and hastens crystallisation, depositing large crystals. Thus, in order to prepare a large crystal of alum, a perfect crystal of alum is suspended into a clear solution of alum by means of a thread from a glass rod. As the solution slowly evaporates the solid deposits on the suspended crystal, which gradually grows in size.

Evaporation of a solution at the ordinary temperature also yields crystals ; thus a solution of sulphur in carbon disulphide deposits pale-yellow rhombic crystals (fig. 23) of sulphur, by the spontaneous evaporation of the volatile solvent.

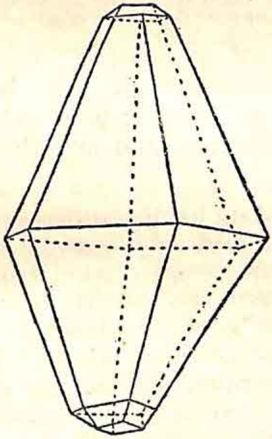


FIG. 23

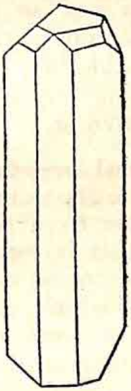


FIG. 24

(ii) by *solidifying certain fused substances :* thus molten sulphur separates out in the form of needle-shaped crystals of monoclinic sulphur on solidification (fig. 24).

(iii) by *condensing the vapours of volatile solids :* thus iodine sublimes on heating giving violet vapours, which condense to the solid directly yielding dark-grey, shining crystals of iodine.

Hydrates and anhydrous substances.—There are many salts which form crystals of definite composition *containing water* ; such crystals are called **hydrates.** The water of hydration is commonly known as **water of crystallisation.** When copper sulphate, for example, deposits in the solid state from its solution in water, it separates in the form of glistening blue crystals of blue vitriol, $CuSO_4$, $5H_2O$, which contains five molecules of water for every molecule of copper sulphate that separates. The water of crystallisation, therefore, forms an essential part of the composition of hydrates. Many salts, while crystallising from their aqueous solutions, separate in the form of hydrates, e.g., blue vitriol, $CuSO_4$, $5H_2O$; green vitriol, $FeSO_4$, $7H_2O$; potash alum, K_2SO_4, $Al_2(SO_4)_3$, $24H_2O$; washing soda, Na_2CO_3, $10H_2O$; Epsom salt, $MgSO_4$, $7H_2O$.

The crystalline shape of the hydrates depends upon their water of crystallisation. A hydrate may be often made *anhydrous* by heating, when the water of crystallisation is driven off ; thus when some crystals of blue vitriol are heated in a test tube, steam is driven off, and the crystals fall to a white powder of *anhydrous* copper sulphate. When moistened, the white substance at once takes up water, and the blue copper sulphate is re-formed. The fact that anhydrous copper sulphate turns blue in presence of a trace of water is used as a delicate test for water.

The pink solution of cobalt chloride is sometimes used as '*invisible*' or '*sympathetic*' *ink*. Any writing done on a paper with weak cobalt chloride solution is practically invisible, but when the paper is held over a small flame the water of hydration of cobalt chloride is driven off, and the letters appear distinctly green or blue.

Water is not an essential part of all crystals. Common salt, $NaCl$, potassium nitrate, KNO_3, potassium chlorate, $KClO_3$, and ammonium chloride, NH_4Cl, are all anhydrous ; these salts crystallise without taking any water of crystallisation, and are, therefore, said to be **anhydrous.**

Fractional crystallisation.—Solids having different solubilities may often be separated from their mixed solutions and obtained in the pure state by a process, called fractional crystallisation. When such a solution is concentrated by heat, and allowed to cool slowly, it first gets saturated with the *least* soluble of the substances in solution, the excess of which, therefore, first deposits as crystals. Thus, when equal parts of common salt and potassium chlorate are dissolved in the minimum quantity of boiling water, and the solution allowed to cool, it is found that the *less soluble potassium chlorate* separates first as crystals. These are filtered off, washed with a little water to dissolve out any adhering common salt, and dried. When not sufficiently pure, the crystals are often purified by re-crystallisation—the crystals are dissolved in a further quantity of boiling water and allowed to stand to cause *re-crystallisation.*

The filtrate, on concentration and cooling, gives crystals of common salt which are similarly filtered, re-crystallised, washed, and dried.

A further crop of crystals is often obtained on slight evaporation of the **mother liquor,** as the filtrate from the first deposit of crystals is commonly called.

The process of crystallisation is very often used in the laboratory to obtain a solid in the pure state—the process may have to be repeated several times before a pure crystalline solid is obtained ; a crystalline solid is characterised by a sharp melting point.

Madame Curie of radium-fame obtained a fraction of a gram of radium salt from a ton of pitch blende by this process of fractional crystallisation.

Efflorescence.—The stability of a hydrate depends on the pressure of water vapour in the atmosphere with which it is in contact. Every hydrate exhibits a definite vapour pressure at the temperature of the room ; when this pressure is greater than the pressure of the water vapour in air, the hydrate in question loses its water of crystallisation, and falls to a powder. Thus, the clear transparent crystals of washing soda, when exposed to the air, become opaque and white and crumble to powder. There is also loss in weight. The change is due to the loss of water from the crystals—washing soda, Na_2CO_3, $10H_2O$, loses 9 molecules of its water of crystallisation and becomes coated with an opaque layer of the monohydrate, Na_2CO_3, H_2O. The washing soda is an efflorescent substance, and the phenomenon is called **efflorescence.**

Efflorescence *is a phenomenon in which a hydrate crumbles to powder, when exposed to the air, due to the loss of all or part of its water of crystallisation.*

Deliquescence.—The vapour pressure of a solution is less than that of pure water—the more concentrated the solution is, the less is its vapour pressure. The vapour pressure of very soluble substances, such as calcium chloride and caustic soda, for example, is very small indeed. It may be even less than the vapour pressure of water vapour in the air : in such a case, the solids, when exposed to the air absorb moisture from the atmosphere and gradually dissolve in it. They are known as deliquescent substances. Thus, when some calcium chloride is put on a watch-glass on the bench, it quickly draws moisture from the air, becomes sticky and finally dissolves. It is a good example of a deliquescent substance. Magnesium chloride, calcium chloride, and caustic soda, etc., are all deliquescent.

Deliquescence *is a phenomenon in which a solid, when exposed to the atmosphere, dissolves in the moisture it absorbs from the air.*

It is worth remembering that pure common salt is not a deliquescent substance. The impure common salt contains small quantities of calcium and magnesium chlorides, and as such it becomes damp or deliquesces, when exposed to the air.

Some substances such as quick lime, glass, porcelain, black copper oxide, and anhydrous copper sulphate, absorb moisture on exposure to the damp air but do not dissolve in it ; these are called **hygroscopic** substances. Deliquescent and hygroscopic substances are consequently kept in closed bottles.

Desiccation.—It is a process of drying, i.e., removing moisture from substances. Deliquescent substances like fused calcium chloride, fused zinc chloride, solid caustic potash, and phosphorus pentoxide, etc., are the usual drying agents. Quick lime and concentrated sulphuric acid are also commonly employed. Silica gel is often used to remove moisture from substances.

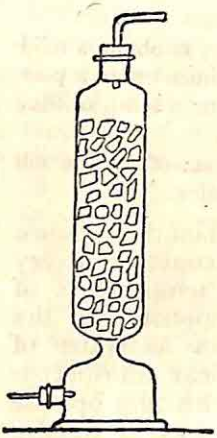


Fig. 25

The *desiccating* agents should be capable of absorbing moisture only but having no chemical action on the substances to be dried.

Gases are usually dried by passing through such drying agents as quick lime, phosphorus pentoxide and fused calcium chloride, etc., contained in *drying towers* (fig. 25) or by sending a stream of gas through *wash bottles* (fig. 26) containing sulphuric acid or a drying tower packed with pieces of pumice soaked in the acid. *Liquids* are best dried by keeping them in contact with a suitable solid drying agent, which is subsequently removed by filtration. *Solids* are dired, according to their nature, in one of the following ways :

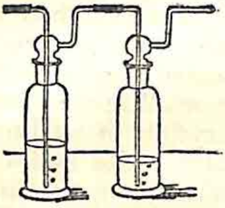


Fig. 26

(a) **At the room temperature** for substances too unstable to be dried by heating. Such substances are dried in a *desiccator* (fig. 27) which is an air-tight thick-walled glass vessel provided with a lid which fits accurately and perfectly air-tight on the upper ground rim of the desiccator, which is greased. The desiccator is contracted at the middle—a circular perforated zinc-sheet placed on a shelf above the constriction, separates the upper from the lower half. The air inside the desiccator is kept dry by putting such drying agents as fused calcium chloride or concentrated sulphuric acid at the bottom. The substance to be dried is kept on a clay-pipe triangle in the upper half. A desiccator not only *dries* a substance but also *prevents it from coming in contact with atmospheric moisture.* Hence hygroscopic substances are kept inside a desiccator after they have been dried by heat.

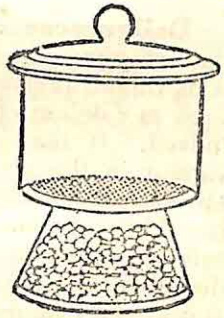


Fig. 27

(ii) **At steam heat.**—Steam oven (fig. 28) is used for drying up to 100°C. It is a double-walled copper vessel with a hinged door and a movable perforated shelf inside. The hollow space between the two walls is partially filled with water through an opening at the top—the water is kept boiling by heating the oven with a gas-burner from below, when the upper portion of the hollow casing is filled with steam. The substance to be dried is put on the shelf inside the oven where the temperature is nearly 100°C.

(iii) **Above steam-heat.**—*Air-oven* (fig. 29) is used for drying above 100°C It is a copper vessel with a hinged door and a movable perforated shelf. The desired temperature is obtained by regulating the gas-burner with which the oven is heated. A thermometer inserted through a cork on the top of the oven records the temperature.

Lixiviation.—Lixiviation refers to extraction, i.e., dissolution of the soluble component of a solid mixture by means of a suitable solvent ; the term is usually used for large extraction only e.g., lixiviation of *kelp or black ash* with water. The term **leaching** also refers to extraction with a solvent.

Some types of chemical reactions.—(i) **Synthesis.**—It is a process in which a compound is formed by direct union of its constituents. Heated sodium burns in chlorine forming sodium chloride. When heated in air, mercury forms mercuric oxide. Water is produced when hydrogen and oxygen are sparked together. Ammonia combines with hydrochloric acid giving ammonium chloride. Carbon dioxide combines with heated quick lime forming calcium carbonate.

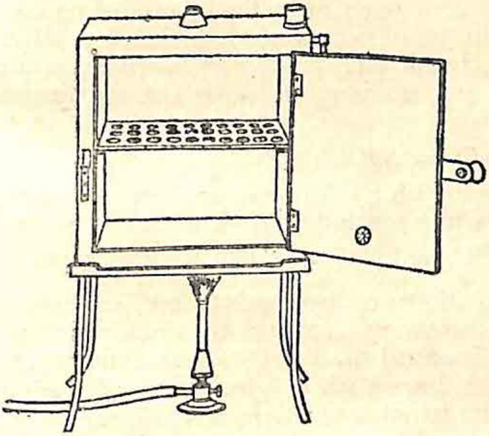


Fig. 28

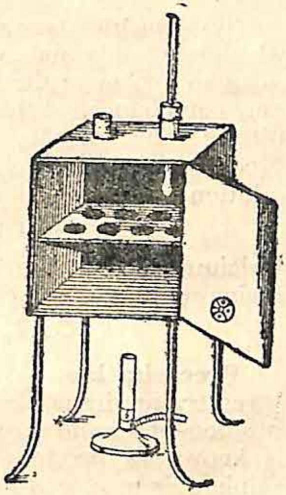


Fig. 29

$$2Na+Cl_2=2NaCl\ ;\ 2Hg+O_2=2HgO.$$
$$2H_2+O_2=2H_2O\ ;\ NH_3+HCl=NH_4Cl.$$
$$CaO+CO_2=CaCO_3.$$

(ii) **Analysis** (also called decomposition).—It is a process in which a compound breaks up into two or more simpler substances. It is thus reverse of synthesis. When strongly heated mercuric oxide decomposes into mercury and oxygen. Acidulated water decomposes into hydrogen and oxygen on electrolysis. Chalk breaks up into calcium oxide and carbon dioxide on heating. Potassium chlorate yields potassium chloride and oxygen on heating.

$$2HgO=2Hg+O_2\ ;\quad CaCO_3=CaO+CO_2$$

$$2KClO_3\text{ (potassium chlorate)}=2KCl\text{ (potassium chloride)}+3O_2$$

(iii) **Displacement.**—It is a process in which one element displaces another from a compound and takes its place. A clean piece of iron dipped in copper sulphate solution gets coated with a red deposit of copper, while iron goes into solution as ferrous sulphate. Zinc displaces hydrogen from sulphuric acid, forming zinc sulphate.

$Fe+CuSO_4$ (copper sulphate) $=Cu+FeSO_4$ (ferrous sulphate).

$Zn+H_2SO_4$ (sulphuric acid) $=H_2+ZnSO_4$ (zinc sulphate).

(iv) **Double decomposition or metathesis**—It is a process in which two compounds, usually acids, bases and salts, react chemically so as to exchange their constituent parts or radicals, produicng two new compounds. When a solution of common salt is added to silver nitrate solution, they react chemically, producing a curdy white precipitate of silver chloride, and sodium nitrate which remains in solution :

$$NaCl+AgNO_3 = AgCl+NaNO_3$$

Calcium chloride solution reacts with a solution of sodium carbonate, giving sodium chloride and a white precipitate of calcium carbonate :

$$CaCl_2+Na_2CO_3 = 2NaCl+CaCO_3$$

Precipitation.—When solutions of two substances are mixed together, an insoluble solid sometimes separate by double decomposition—the solid separating is called the precipitate and the process is known as precipitation. A heavy white precipitate of barium sulphate is produced by mixing together solutions of barium chloride and sulphuric acid :

$$BaCl_2 + H_2SO_4 = BaSO_4 + 2HCl$$

A black precipitate of copper sulphide is produced by passing a stream of hydrogen sulphide gas into copper sulphate solution :

$$CuSO_4 + H_2S = CuS + H_2SO_4$$

When hydrogen chloride (HCl gas) is passed into a saturated solution of common salt, pure sodium chloride, NaCl, precipitates out in the form of colourless transparent crystals.

(v) **Hydrolysis.**—A compound is said to undergo hydrolysis when it is split up by water, either completely or partially, producing new substances.

$$PCl_3 + 3H_2O = H_3PO_3 \text{ (phosphorous acid)} + 3HCl$$

$$Na_2CO_3 + H_2O \leftrightharpoons NaHCO_3 \text{ (sodium bicarbonate)} + NaOH$$

The Colloidal State.—In course of his investigations on diffusion of solutions of various substances, Thomas Graham (1852-60) observed that acids, bases and salts could readily diffuse in solution and fairly quickly pass through vegetable and animal membranes, whereas substances like glue, starch and albumen diffused but very slowly. The rapidly diffusing substances were called by Graham **crystalloids**, since most of them were crystalline in the solid state. Albumen, starch, gum, proteins, etc., on the other hand, which form amorphous solid masses resembling glue, were called **colloids** from the Greek word *kolla*, meaning glue, which was a typical member of the group of substances that diffused very slowly. Graham thus differentiated between "two classes of matter, the crystalloid and the colloid," each with characteristic properties.

But in the light of later researches it is more correct to speak of the *colloidal state of matter* than to describe a substance as a colloid or crystalloid, since most substances may be obtained in the colloidal state under suitable conditions. Common salt, for example, which is a typical crystalloid in aqueous solution, may be brought into a colloidal state in benzene ; soap, which forms a colloidal solution in water, behaves as a crystalloid in alcoholic solution. It is the *size of the particle* which decides if a substance will remain in the colloidal state. The term colloid, therefore, refers not so much to a class of substance as to a *state of subdivision.*

In a true solution, such as one of common salt or sugar in water, the solute distributes in the solvent as ions or single molecules. A suspension, on the other hand, contains particles which are visible to the naked eye or, at least, in a microscope. Between these two extremes exists the *colloidal system in which the particles are larger than molecules but are not large enough to be seen under the microscope.* A coarse suspension, a colloidal solution and a true solution differ as regards *size of particles only. Size of particles :*

Coarse suspension	Colloidal particle	Molecular diameter
10^{-4} cm	10^{-5} to 10^{-7} cm	10^{-8} cm

Dialysis.—Colloids may be separated from crystalloids by a process, called dialysis. *Dialysis is a process of separation of a colloid from a crystalloid from a mixture of the two in solution by diffusion through a membrane, such as parchment paper and collodion film, which lets through the crystalloid but not the colloid.*

Experiment.—A solution of starch and potassium iodide is taken in a bell jar, over the mouth of which a piece of parchment paper is tightly tied—the apparatus is called a **dialyser** (fig. 30). It is suspended in a jar of distilled water, so that the parchment paper dips into the water. After sometime, about half an hour, chlorine water is added to the water in the outer jar—a *yellow colour* due to liberated iodine shows that the crystalloid potassium iodide has passed through the parchment paper, but the starch is retained, which would, otherwise, have given a blue colour with the iodine ; on adding both chlorine water and starch into outer jar, blue colour develops, showing that potassium iodide alone did diffuse out.

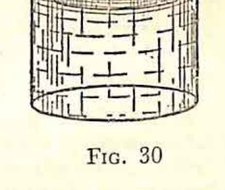


FIG. 30

Colloidal solution.—Unlike a true solution which is homogeneous, *a colloidal solution is heterogeneous* and consists of two phases, one of which is distributed throughout the other as small particles or droplets ; the substance that is in the form of particles or droplets is in the *colloidal state* and is known as the *dispersed phase*, and the medium in which the particles are distributed (or dispersed) is called the *dispersion medium.*

The dispersed phase and the dispersion medium may be solid, liquid or gas, except that two gases cannot form a colloidal system. When the dispersion medium is a liquid, the colloidal systems are called *sols ;* sometimes the sols are as thick as jelly and are called *gels. Smoke* and *dust* consist of solid particles dispersed in a gaseous medium, whereas in *fog, mist* and *cloud* a liquid is dispersed in a gas. A *foam* consists of a gas dispersed in a liquid ; one liquid is dispersed as droplets in another liquid in an *emulsion*, e.g., milk is an emulsion of fat in water ; when a solid of relatively large particle size is distributed in a liquid the result is a *suspension*, e.g., suspensions of fine particles of clay, flour, etc., in water.

Properties of sols.—(i) **Diffusion and dialysis.**—The rate of diffusion of a sol is very much less than that of a solute in true solution. The process of purifying a sol from true solution, known as *dialysis*, depends largely on the differential rates of diffusion.

(ii) **Optical properties.**—(a) **Tyndall effect.**—Colloidal particles are too small to be seen in a microscope. But just as dust particles in the path of light when a sun beam enters a dark room, become visible due to scattering of light from their surface, so also when a strong beam of light is passed through a sol in a darkened room, the individual colloidal particles scatter light and as a result they appear as flashes of light which can be observed and counted under a *ultra-microscope*, first constructed and used by Zsigmondy. The colloidal solutions, thus scatter light, producing what is called Tyndall effect. A true solution does not show Tyndall effect and is said to be optically void.

(b) **Brownian movement.**—When observed in the ultra-microscope colloidal particles are found to undergo a ceaseless random motion, referred to as Brownian movement after the name of English botanist Robert Brown who in 1827, first observed this movement in pollen grains dispersed in water. The Brownian motion is due to the impact of the molecules of the medium on the colloidal particles.

The Tyndall effect and Brownian motion are characteristics of colloidal solutions only.

(iii) **Electrical properties.**—(a) **Electrophoresis and electro-osmosis.** When a sol is placed in an electric field, colloidal particles move in one direction or another, showing that *the colloidal particles are electrically charged with respect to the dispersion medium.* When two platinum wires connected to the terminals of a battery, for example, are dipped in arsenic sulphide sol in a U-tube, the colloidal particles slowly move towards the positive pole, showing that they carry negative charges. This phenomenon of movement of colloidal particles under the influence of an electrical potential is called *electrophoresis ;* also called *cataphoresis*.

Colloidal particles of clay, arsenious sulphide, silicic acid and metals such as Au, Ag and Pt, carry negative charges, whereas haemoglobin, and metallic hydroxides, e.g., $Fe(OH)_3$ and $Al(OH)_3$, etc. are positively charged.

When an electric field is applied to a sol under condition in which the colloidal particles are held stationary the liquid is observed to move—this effect is known as *electro-osmosis*, when the colloidal particles are negatively charged, the liquid moves towards the negative pole.

(b) **Coagulation of colloids.**—Electrical charge is an important factor in the stabilisation of colloids. When an electrolyte is added to a colloidal sol, the latter slowly gets turbid and finally the dispersed phase separates out as a precipitate : this phenomenon is known as *precipitation or coagulation*. Coagulation is due to the neutralisation of the charge on the colloid particles by the oppositely charged ions of the added electrolyte. The coagulating power of an electrolyte depends upon the valency of its ions. **Hardy—Schulze rule** states that (i) the *ion which is effective in causing coagulation of a sol is the ion whose charge is of opposite sign to that of colloidal particles*, and (ii) *the coagulating power increases with increasing valency of the ion.* Bivalent sulphate ions, for example, are about 50 times more effective than univalent chloride or nitrate ions in coagulating positively charged ferric hydroxide sol. Charged colloids are also effective in coagulating colloids of opposite charge ; when positive ferric hydroxide sol and negative arsenious sulphide sol are mixed, mutual coagulation of two colloids take place. Heating a sol also favours coagulation.

The phenomena of electrophoresis and electro-osmosis, and coagulation are characteristics of sols only.

Exercises

1. What do you understand by the terms *solution* and *solubility* ?

Describe fully how you would determine the solubility of potassium nitrate at the temperature of the room. Why is it necessary to specify the temperature while referring to the solubility of a substance ?

2. Explain the terms *saturated solution* and *super-saturated solution.* How does a solution differ from a compound ?

One hundred grams of water dissolve the following weights of ammonium chloride at the temperature named :

Temperature	0°	10°	20°	30°	40°	50°	60°	80°	100°
Substance	28.4	32.8	37.3	41.4	46.2	50.6	55.0	64.0	72.8 gram.

Construct the solubility curve of the substance, and from the curve determine the solubility of ammonium chloride at 24° and 70°.

What information can be obtained from the study of solubility curve ?

3. What is meant by (*i*) crystal, (*ii*) *crystallisation*, (*iii*) water of crystallisation ? *P. U.* 1962.

Given a mixture of common salt and potassium nitrate, how would you obtain pure specimens of both the materials ?

4. Explain the terms (i) *efflorescence* and *deliquescence*, (ii) *hydroxide* and *hydrate*. Illustrate your answer with suitable examples.

How would you find out if washing soda is efflorescent or deliquescent ?

5. Explain fully what is meant by (a) *distillation*, (b) *sublimation*.

How would you separate a mixture of ammonium chloride and common salt ?

A sample of muddy water is provided. How would you find if the water contained any dissolved salt in it, and how would you obtain a sample of pure water from it ?

6. Describe how you would separate the ingredients in each of the following, noting the properties of the ingredients which help you in separating them : (i) a mixture of common salt and nitre ; (ii) a mixture of silver chloride and lead chloride ; (iii) a mixture of iron filings and sulphur ; (iv) a mixture of sand and chalk.

7. How would you separate :

(i) a mixture of sand, chalk, and common salt,

(ii) a mixture of iodine, sodium sulphate and sand,

(iii) a mixture of iodine, common salt, and powdered glass.

(iv) a mixture of hydrogen and carbon dioxide.

(vi) gunpowder into its constituents ?

How would you prove that the gunpowder is a mixture ?

8. Explain the terms *analysis* and *synthesis*. Illustrate your answer with examples. How would you separate water into its constituents ?

9. What are colloids and crystalloids ? Give examples. What is dialysis ? Cal. '58

10. What is meant by a colloidal solution ? How it differs from a true solution ?

VI

BOYLE'S LAW AND CHARLES'S LAW

The laws governing the behaviour of gases under different conditions of temperature and pressure are, to a large extent, independent of the nature of the gas. Boyle's law (1662) states the effect of pressure on the volume of a gas. The law of variation of volume of gas with temperature was stated by Gay Lussac in 1802 but often called Charles's law, since similar results were obtained by Charles in 1787, although they were not published at that time.

Boyle's Law.—*At constant temperature, the volume of a given mass of any gas is inversely proportional to the pressure.* In other words, if pressure is brought to bear upon a known volume of a gas, this volume will decrease as the pressure increases, and *vice versa.*

If the pressure on a gas, for example, is doubled, its volume will be reduced to one-half of what it was originally. Mathematically, Boyle's law may be stated in the form :

temperature remaining constant, $v \propto 1/p$, or $pv=k$,

where p is the pressure and v the volume of the gas, and k is a constant.

If p_1 and v_1 are the pressure and volume of a given mass of a gas and p_2 and v_2 are the pressure and volume of the same amount a the gas consequent to some change in initial pressure or volume, then :

$$p_1v_1 = k \text{ and } p_2v_2 = k, \text{ so that } p_1v_1 = p_2v_2$$

Boyle's law is also known as Marriotte's law.

Charles's law.—*At constant pressure, the volume of a given mass of any gas expands by* 1/273 of its volume at 0°C *for each* 1°C *rise in temperature.*

Stated in the symbols,

$$v_1=v+v.\frac{t_1}{273}=v\left(1+\frac{t_1}{273}\right)=v\frac{273+t_1}{273}$$

where v is the initial volume of the gas at 0°C, and v_1 is the volume after the temperature has been raised to t_1°C.

It is found that when $t_1=-273$°C, the volume becomes zero, that is, if a gas were cooled to −273°C, it would have occupied no volume at that temperature, which is called the **absolute temperature.** The absolute temperature is obtained by taking −273°C as zero degree absolute. This is denoted by T.

Thus, 0°C = 273° absolute ; t°C$=(t+273)$° absolute.

Let v_1 and v_2 be the volumes of a given mass of a gas at temperatures t_1°C and t_2°C respectively ; then :

$$v_1 = v\left(\frac{273+t_1}{273}\right) \text{ and } v_2=v\left(\frac{273+t_2}{273}\right)$$

$$\therefore \quad \frac{v_1}{v_2} = \frac{273+t_1}{273+t_2} = \frac{T_1}{T_2}, \text{ i.e., } \frac{v}{T} = \text{constant.}$$

Consequently, $v \propto T$, when pressure remains constant.

The volume of a given mass of any gas at constant pressure, therefore, *is directly proportional to its absolute temperature.* This is an alternative expression for Charles's law.

Equation of state.—The results of Boyle's law and Charles's law may be combined in an expression giving a relation between temperature, pressure and volume of a given mass of a gas—such an equation is known as an equation of state.

Since for a given mass of a gas :

(i) $v \propto 1/p$, when T remains constant (Boyle's law) ;

(ii) $v \propto T$, when p remains constant (Charles's law) ;

$\therefore$ $v \propto T/p$, when both T and p vary.

$$\therefore \quad v = k\frac{T}{p}, \text{ where k is a constant, i.e., } \frac{pv}{T} = \text{constant}$$

for given mass of a gas.

This equation of state, pv/T = constant, implies that for a given mass of gas, any change of temperature and pressure would cause a corresponding change in volume, so that the quantity pv/T remains constant.

If p_1, v_1, T_1 and p_2, v_2, T_2 are the pressure, volume and temperature of a given mass of a gas under two sets of conditions, then :

$$\frac{p_1v_1}{T_1} = \frac{p_2v_2}{T_2}$$

This equation enables us to find out the volume of a given mass of gas if its temperature and pressure are changed.

Density of gas.—Density of a gas is the mass per unit volume.

Stated in symbols, $d = w/v$, or $w = v \times d$,

where w is the mass, v the volume and d the density of gas.

At constant temperature the density of a given mass of gas is inversely proportional to its volume, i.e., if the volume increases, the density will correspondingly decrease, i.e., $d \propto 1/v$.

Now, at contant temperature $v \propto 1/p$; hence *at constant temperature density of given mass of gas is directly proportional to pressure,*

i.e., T remaining constant, $d \propto p$.

Again, at constant pressure $v \propto T$; hence, p remaining constant, $d \propto 1/T$.

$\therefore$ $d \propto p/T$ where both T and p vary, i.e., $d = \text{constant} \times p/T$.

$\therefore$ p/dT=contant, $\therefore$ $P_1/d_1T_1 = p_2/d_2T_2$.

The density of a gas, also called its **normal density,** is the weight in grams of 1 litre measured at a temperature of 0°C, and under a pressure of 760 mm. of mercury.

One litre of hydrogen at N.T.P. weighs 0.089873 *gram.*

Normal temperature and pressure.—In order to compare the results on gaseous volumes measured under different conditions it is necessary to refer to some standard conditions of temperature and pressure under which the volumes are reduced. These standard data are 0°C and a pressure of 760 mm. of mercury. They are called *standard* (or *normal*) *temperature* and *pressure*, and are generally written as *S.T.P.* (or N.T.P.)

Dalton's law of partial pressures.—In a mixture of gases which do not react chemically, the total pressure exerted by the mixture is the sum of the *partial pressure* of each gas—the partial pressure is the pressure each gas would exert if it were *separately* confined in the entire volume occupied by the mixture. This is Dalton's law of partial pressures.

Suppose a vessel of volume v contain two gases A and B under a pressure p and at a given temperature T. Let p′ and p″ be the partial pressures of the two gases, i.e., $p = p' + p''$.

$v = v_1$ (volume of gas A) $+ v_2$ (volume of gas B).

By Boyle's law, $p'v = pv_1$, and $p''v = pv_2$,

$$\therefore\ p' = \frac{v_1}{v}p = \frac{v_1}{v_1+v_2}p\ ;\ p'' = \frac{v_2}{v}p = \frac{v_2}{v_1+v_2}p$$

Pressure of gases collected over water.—When a gas is collected over water in a jar, the total pressure inside the jar is equal to the atmospheric pressure, when the levels of water inside and outside the jar are the same. Since the gas collected is *moist and saturated with water vapour* i.e., it is a mixture of gas and water vapour, the atmospheric pressure (P mm. of mercury) is equal to the sum of the partial pressure of the dry gas (p mm. of mercury) and the partial pressure of saturated water vapour, also known as aqueous tension (f mm. of mercury) at the temperature at which the gas is collected.

Stated in symbols, $P = p + f$; $\therefore\ p = (P - f)$, i.e., pressure of dry gas = atmospheric pressure − aqueous tension at t°C.

t°C is the temperature at which the gas is collected.

Let the volume of a moist gas at t°C = v c.c. ;
the barometric pressure = P mm. of mercury ;
the aqueous tension at t°C = f mm. of mercury.

∴ the pressure of dry gas = (P − f) mm. of mercury.

Let the gas occupy a volume of v′ c.c. at N.T.P., then by Boyle's law,

$$\frac{v' \times 760}{273} = \frac{v\ (P-f)}{273+t},\ \text{or}\ v' = \frac{v.(P-f).273}{(273+t).760}$$

Another case arises when the levels of water inside and outside the jar are not the same. Suppose the water stands at a height h mm. above the water in the trough, then the atmospheric pressure = the pressure of dry gas + the aqueous tension + the pressure of h mm. of water. Symbolically stated, $P = p + f + h/13.59$, since the density of mercury is 13.59 gm. per c.c.

$$\therefore\ p = (P - f - h/13.59).$$

Diffusion of gases.—The molecules of a gas are not in a state of rest ; they are in a state of ceaseless chaotic motion. When some chlorine gas is led into the bottom of a gas-jar (which presumably contains air), it is found that the gas quickly spreads out into the jar so that its contents appear uniformly greenish yellow, although it is about two and a half times as heavy as air ; this is because its molecules are in rapid and random motion.

When a gas-jar is filled with hydrogen and held mouth downwards, the hydrogen rapidly passes out and air enters, as is evident from the observation that if a lighted taper is applied to the jar, it is found that no trace of the gas remains—the hydrogen, if present, would have burnt with a pale blue flame. This is another illustration of the random motion of the molecules ; the movement has taken place in opposition to gravity, since air, the heavier gas, moves upward and hydrogen, the lighter gas, moves downward.

Exactly for the same reasons, when a jar of hydrogen is inverted over a jar of carbon dioxide which is twenty-two times as heavy as hydrogen, the molecules of the two gases so intermix together that a perfectly uniform mixture is obtained. *Such an intermixture of different non-reacting gases without the aid of outside agencies is due to the perpetual random motion of their molecules, and is known as the phenomenon of diffusion.* Regardless of densities, all gases possess the property of diffusion ; the phenomenon of diffusion is independent of gravity.

The foul smell of hydrogen sulphide in a chemical laboratory is an unmistakable proof of its diffusion in air. It is diffusion that spreads the fragrance of flowers. Tear gas pervades a locality while used in dispersing a chaotic mob.

Graham's law of diffusion.—A light gas diffuses more rapidly than a heavy gas.

At a given temperature and pressure the rate of diffusion of a gas is inversely proportional to the square root of its density.

Thus, oxygen is 16 times as heavy as hydrogen, and therefore diffuses $\sqrt{16}=4$ times as slowly.

Carbon dioxide is 22 times as heavy as hydrogen, and therefore diffuses $\sqrt{22}=4.69$ times as slowly.

Mathematically, the law is stated as : $r \propto 1/\sqrt{d}$.

Consequently, $\frac{r_1}{r_2}=\sqrt{\frac{d_2}{p_1}}$

where d_1 and d_2 are the densities of two gases, for which the rates of diffusion under identical conditions are r_1 and r_2.

The rate of diffusion means the volume-rate, and is measured by the volume of a gas diffusing per unit of time, and is usually expressed as :

$$\text{rate of diffusion}=\frac{\text{volume of diffused gas in c.c}}{\text{time in seconds}}$$

Experiment illustrating diffusion.—The prenomenon of diffusion may be demonstrated with the following experiment.

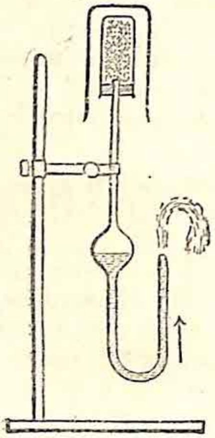


FIG. 31

A porous clay pot is fitted by means of a rubber bung to the longer limb of a bent tube containing some coloured liquid, such as a solution of potassium permanganate—the shorter limb of the tube ending in a fine jet (fig. 31). On inverting a beaker full of hydrogen over the porous pot, it is found that the coloured liquid spurts out through the jet in the form of a fountain. The explanation is simple. The molecules of hydrogen, the lighter gas, diffuse into the pot more rapidly, and therefore in large numbers, than the molecules of air, the heavier gas, pass out ; consequently, there occurs an increase of pressure inside the pot, and hence the liquid is forced out.

Effusion of Gases.—Effusion is a process in which a gas is forced under pressure through a small aperture in a thin metal plate exposed to the air.

Graham's law applies equally to the rates of diffusion and effusion. The law holds good whether the gas densities are expressed as normal or relative densities.

Since twice the relative density of any gas is its molecular weight.

$$\frac{r_1}{r_2}=\sqrt{\frac{d_2}{d_1}}=\sqrt{\frac{M_2}{M_1}}$$

where M_1 and M_2 are the molecular weights of the two gases.

Exercises

1. A gas occupies 100 c.c. at a pressure of 340 mm. of mercury. What will be the volume at a pressure of 1000 mm., assuming the temperature to be constant ?

We use Boyle's law : pressure × volume = constant ;

$\therefore\ 100\times340 = 1000\times x$, whence $x = 34$ c.c.

2. A litre of gas is measured at 20°C. At what temperature will its volume be 1750 c.c. ?

We use Charles's law : $\frac{v_1}{T_1}=\frac{v_2}{T_2}$;

$v_1 = 1000$ c.c. ; $T_1 = 273+20 = 293$; $v_2 = 1750$ c.c. ; $T_2 = x$.

$\therefore\ \frac{1000}{293}=\frac{1750}{x}$ or $= 512.8°$ absolute.

Let the temperature be t°C, then

$T_2 = (273+t)°$ absolute $= 512.8°$ abs. or $t = 239.8°C$.

3. Correct a volume of 234 c.c. measured at 756 mm. and 12°C to standard conditions.

Standard temperature is 0°C=273° absolute.
Standard pressure is 760 mm. of mercury.

We apply the general gas equation : $\frac{p_1v_1}{T_1}=\frac{p_2v_2}{T_2}$

$p_1=756$ mm. ; $v_1 = 234$ c.c. ; $T_1 = 273+12 = 285$;

$p_2 = 760$ m.m. ; $v_2 = x$; $T_2 = 273$;

$\therefore\ \frac{756\times234}{285}=\frac{v_2\times760}{273}$ whence $v_2 = 223$ c.c.

4. 110 c.c. of hydrogen were collected over water at 18°C and 740 mm. pressure. Calculate the volume of the gas at N.T.P. (a) taking account of pressure of water vapour (15.4 mm. at 18°C), (b) neglecting the effect of the water vapour.

(*a*) From the relation $\frac{v_1\,760}{273}=\frac{v(P-f)}{(273+t)}$

$$v_1 = \frac{v(P-f)273}{(273+t)760}=\frac{110.(740-15.4)273}{(273+18)760} = 98.4 \text{ c.c.}$$

(*b*) $\frac{v_1.760}{273}=\frac{v.P}{(273+t)}$ (aqueous tension neglected)

$$\therefore \quad v_1 = \frac{v.P.273}{(273+t).760}=\frac{110.740.273}{(273+18).760}=100.5 \text{ c.c.}$$

5. If the density of hydrogen is 0.09 gm. per litre at N.T.P., what is the density at 15°C and the pressure 750 mm. ?

$$\frac{P_1v_1}{T_1}=\frac{P_2v_2}{T_2} \text{ becomes } \frac{P_1}{d_1T_1}=\frac{P_2}{d_2T_2}$$

$$\therefore \frac{760}{0.09\times273}=\frac{750}{d_2\times(273+15)}, \text{ whence } d_2 = 0.0842 \text{ gm. per litre.}$$

6. A gas is collected over water in a jar. The volume measured is 270c.c. The height of water in the jar is 2.72 cm. The temperature of gas is 27°C. Aqueous tension at 27°C is 26.75 mm., and atmospheric pressure is 750.75 mm. Calculate the volume of the gas at N.T.P. Density of mercury is 13.6 gm. per c.c.

Pressure of water column in the jar = 27.2/13.6 = 2 mm.

∴ Pressure of *moist* gas collected = 756.75 − 2 = 754.75 m.m.

∴ pressure of *dry* gas = 754.75 − 26.75 = 728 mm.

$$\therefore \frac{v\times760}{273}=\frac{270\times728,}{(273+27)} \quad \text{or } v = 235.4 \text{ c.c.}$$

7. 24 c.c. of air diffuse through a porous membrane in 18 seconds. 21 c.c. of carbon dioxide diffuse through the same membrane in 19.5 seconds. Find the density of carbon dioxide, that of air being 14.4

Let u_1 = speed of diffusion of air = 24/18 c.c. per second,
and u_2 = speed of diffusion of carbon dioxide = 21/19.5 c.c. per second.

But $\frac{u_1}{u_2}=\frac{\sqrt{d_2}}{\sqrt{d_1}}$ where d_1 and d_2 are the densities of air and carbon dioxide respectively.

$$\therefore \frac{d_2}{d_1}=\left(\frac{u_1}{u_2}\right)^2, \quad \text{whence } d_2 = 14.4\times\left(\frac{24\times19.5}{18\times21}\right)^2=22{\cdot}07.$$

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8. A certain volume of nitrogen at N.T.P. is heated to 177°C, the volume being not allowed to change. Calculate the new pressure. 1252 mm.

9. A quantity of gas occupies a volume of 10 litres at N.T.P. What is its volume at 100°C and 800 mm. pressure ? 12.98 litres.

10. Deduce from Boyle's and Charles's laws the relation pv/T is a constant. A given mass of a gas occupies a volume of 1000 c.c. at 27°C and 760 m.m. pressure of mercury. What volume will it occupy at 327°C and 1520 mm. pressure of mercury ? *Cal.* '52 ; 1000 c.c.

11. 50 c.c. of nitrogen are collected over water at 30°C and at a pressure of 740 mm. of Hg. Aqueous tension at 30°C is 31.6 mm. Calculate the volume of dry nitrogen at N.T.P. 42 c.c.

12. 228 c.c. of oxygen are collected over water in a jar at 15°C. The height of water in the jar above that in the trough is 6.8 cm. and the barometric pressure is 734 mm. Correct the volume at N.T.P. The density of mercury is 13.6 gm. per c.c. and aqueous tension at 15°C is 13 mm. 203.6 c.c.

13. The pressure on 12 c.c. of a gas is 7 atmospheres; it is then reduced to 847 mm. Find the new volume. At what temperature will a litre of air weigh 1 gm.? At 0°C 1 litre of air weighs 1.293 gm. 75.37 mm.; 80°C.

14. 2.096 litres of a gas at 17°C and 770.2 mm. weigh 3.93 gm. What is the weight of 1 litre of the gas at N.T.P.? 1.965 gm.

15. Establish the relation between temperature, pressure and volume of a gas.

A cylinder of oxygen contains 50 litres of the gas under a pressure of 120 atmospheres. Calculate the number of gas jars, each of 500 c.c. capacity, which could be filled up from the cylinder when the atmospheric pressure is 760 mm. 11900.

16. 100 c.c. of hydrogen are measured at 100°C. How many c.c.'s will the gas occupy at −100°C? 46.37 c.c.

17. 1 litre of chlorine at N.T.P. weighs 3.2 gm. Calculate its molecular weight. 1 gm. molecule occupies 22.4 litres at N.T.P. What do 100 litres of nitrogen at N.T.P. weigh? 71.68 g.; 125 gm.

18. 2.16 gm. of a solid when heated gave off 125 c.c. of oxygen at 15°C and 754 mm. The gas was collected over water. If the pressure of saturated water vapour is 12.7 mm. at 15°C, find what volume of dry oxygen at N.T.P. would be given off by 1 gm. of the solid. 53.5 c.c.

19. 125 c.c. of a gas at N.T.P. weighs 0.1563 g. What is the molecular weight of the gas?. 28

20. 0.1 g. of a gas occupies 77.94 c.c. at 27°C and 750 mm. pressure. Calculate its molecular weight. 32

21. If 347.2 c.c. of hydrogen diffuse through a crack in 10 seconds, how much ethylene (density 14) will diffuse in the same time? 100 c.c.

22. Explain what is meant by diffusion of gases. State Graham's law of diffusion The speeds of diffusion of carbon dioxide and ozone were found by Soret to be 0.29 : 0.27. Determine the density of ozone, that of carbon dioxide being 22. Allahabad, '46; 25.37.

23. In 50 seconds 300 c.c. of oxygen diffuse through a porous plate. How long will it take 500 c.c. of chlorine to diffuse through the same plate? Take the molecular weights of oxygen and chlorine to be 32 and 72 respectively. 125 *seconds*.

VII

THE LAWS OF CHEMICAL COMBINATION AND DALTON'S ATOMIC THEORY

As a result of the *quantitative* study of chemical changes the following laws relating to the combination of elements by weight, or what are known as *laws of stoichiometry* (**Laws of Chemical Combination**) were discovered :

(i) *The law of conservation of mass*, (ii) *The law of constant proportions*, (iii) *The law of multiple proportions*, (iv) *The law of reciprocal proportions.*

Combination of elements to form compounds and chemical reactions in general are governed by these laws. These laws are purely experimental and are not based on any theory.

The law of conservation of mass.—The law was experimentally arrived at by Lavoisier in 1774. The law states :

In a chemical change the total mass of the reacting substances is equal, within the limits of experimental error, to the total mass of the products of the reaction (*page* 6).

Since there is no gain or loss of matter accompanying a chemical change, every correctly balanced chemical euqation is based on this law.

The law of constant proportions, also called **the law of definite proportions,** was discovered by the French chemist Proust in 1799. The law states :

The same compound always contains the same elements combined together in the same definite proportion by weight.

Irrespective of any method of preparation or source, water always contains the elements hydrogen and oxygen only, in the same proportion of 1.008 to 8 parts by weight ; common salt does contain the elements sodium and chlorine only—always in the ratio of 23 to 35.5 parts by weight ; carbon dioxide is made up of the elements carbon and oxygen only and always in the fixed ratio of 3 to 8 parts by weight. Since elements combine in definite ratios by weight, *the composition of a pure chemical compound is definite* and is independent of its method of preparation.

The law is implied in the very definition of a chemical compound.

The law has been verified by preparing the same compound in different ways and analysing the samples obtained. Different samples of black cupric oxide has been found to contain in each case copper and oxygen in the ratio of 63.57 to 16 parts by weight, on analysis. Similarly, analysis of different samples of silver chloride shows that it contains silver and chlorine in the ratio of 107.88 to 35.457 by weight.

The law of multiple proportions.—This law was arrived at by Dalton in 1803 as a result of some theoretical reasoning about gases. The law states :

When two elements combine to form more than one compound, the several weights of one element which combine with a fixed weight of another element are in the ratio of small whole numbers.

Illustrations.—(i) Let us consider water and hydrogen peroxide. In water H_2O, 1.008 parts by weight of hydrogen combine with 8 parts by weight of oxygen ; in hydrogen peroxide, H_2O_2, 1.008 parts by weight of hydrogen combine with 16 parts by weight of oxygen. Hence, the same weight, 1.008 parts by weight of hydrogen unite with 8 and 16 parts by weight of oxygen in water and hydrogen peroxide respectively. 8 and 16 are in simple ratio of 1 : 2.

Compound	*Composition by weight*		*Simple ration of oxygen*
	Hydrogen	Oxygen	
Water	1.008	8	
Hydrogen peroxide	1.008	16	1 : 2

(ii) In the five oxides of nitrogen, nitrous oxide, nitric oxide, nitrogen trioxide, nitrogen tetroxide and nitrogen pentoxide, the weights of oxygen combining with a definite amount of nitrogen are in the ratio of 1 : 2 : 3 : 4 : 5.

Oxides of nitrogen	*Composition by weight*	
	Nitrogen	Oxygen
Nitrous oxide, N_2O	14	$8(1\times8)$
Nitric oxide, NO	14	$16(2\times8)$
Nitrogen trioxide, N_2O_3	14	$24(3\times8)$
Nitrogen tetroxide, N_2O_4	14	$32(4\times8)$
Nitrogen pentoxide, N_2O_5	14	$40(5\times8)$

(iii) In the following hydrides of carbon, acetylene, ethylene ethane and methane, 12 parts by weight of carbon combine with 1.008, 2×1.008, 3×1.008, and 4×1.008 parts of hydrogen respectively—these weights are in the ratio of 1 : 2 : 3 : 4.

Compound	*Composition by weight*	
	Carbon	Hydrogen
Acetylene, C_2H_2	12	1×1.008
Etheylene, C_2H_4	12	2×1.008
Ethane, C_2H_6	12	3×1.008
Methane, CH_4	12	4×1.008

(iv) The two oxides of copper, namely black cupric oxide and red cuprous oxide, illustrate the law.

Compound	*Composition by weight*		*Simple ratio of copper*
	Oxygen	Copper	
Cupric oxide, CuO	16	63.57	1 : 2
Cuprous oxide, Cu_2O	16	63.57×2	

The law of reciprocal proportions.—The law was discovered by Richter in 1792, and is also called **the law of equivalent proportions** or **the law of combining weights.** The law states :

The weights of two or more elements which combine separately with a fixed weight of another element, are either the weights in which these elements combine with one another or are simple multiples of them.

In other words, the proportions in which any two elements unite with a third element are the proportions or a simple multiple or submultiple of the proportions in which they combine with each other.

Illustrations.—(*i*) Let us consider hydrogen, sodium, chlorine and their compounds sodium hydride, hydrogen chloride and sodium chloride.

Compound	*Composition by weight*	*Ratio of equivalents*
Sodium hydride, NaH	H : Na = 1 : 23	Na : Cl = 23 : 35.5
Hydrogen chloride, HCl	H : Cl = 1 : 35.5	
Sodium chloride, NaCl	Na : Cl = 23 : 35.5	

With respect to combination with hydrogen, the equivalents of sodium and chlorine are 23 and 35.5 respectively. Sodium and chlorine should, therefore, combine in the ratio of 23 : 35.5. In sodium chloride the ratio is 23 : 35.5.

(*ii*) Consider the elements carbon, hydrogen and oxygen.

Compound	*Composition by weight*	*Ratio of equivalents*
Methane, CH_4	H : C = 1 : 3	C : O = 3 : 8
Water, H_2O	H : O = 1 : 8	
Carbon dioxide, CO_2	C : O = 3 : 8	
Carbon monoxide, CO	C : O = 3 : 4	

The equivalents of carbon and oxygen are 3 and 8 respectively. Carbon and oxygen should combine in the ratio of 3 : 8 by weight or in simple multiple or submultiple of this ratio. In carbon dioxide the ratio is 3 : 8 and in carbon monoxide it is 3 : 4 (4 is a submultiple of 8).

(*iii*) The following compounds also illustrate the law :

Compound	*Composition by weight*	*Ratio of equivalents*
Carbon dioxide, CO_2	C : O = 3 : 8	C : S = 3 : 8
Sulphur dioxide, SO_2	S : O = 8 : 8	
Carbon disulphide, CS_2	C : S = 3 : 16	

Carbon and sulphur should combine in the ratio of 3 : 8 or in their simple multiples ; in carbon disulphide the ratio is 3 : 16 ; 16 (2×8) is a multiple of 8.

The atomic theory.—It has been vaguely supposed from very early times by the ancient Hindu philosopher Kanad and the Greek philosophers Leukippos and Demokritos (about 450 B.C.) that matter is composed of very minute indivisible particles, called atoms. Their metaphysical speculation was developed by the English scientist John Dalton in 1803 into a scientific theory which asserts that :

(i) All elements are composed of very minute particles of matter called atoms, which remain undivided in all chemical changes.

(ii) Each kind of atom has a definite weight, but the atoms of different elements differ in weight.

(iii) All the atoms of the same element are identical with one another in all respects, particularly in weight.

Atoms of different elements are themselves different having different properties, such as weight, chemical affinity, etc.

JOHN DALTON (1766—1844).
Fig. 32

(iv) Chemical combination takes place by the union of atoms of the elements in simple numerical ratios, 1 : 1, 1 : 2, 2 : 3, *etc.*

The atom, therefore, is the smallest particle of an element which can take part in a chemical change.

It is not out of place to mention here that according to the original assumption of Dalton's atomic theory an atom was the smallest particle of all kinds of matter, be it an element or a compound. The smallest particle of an element was called a '*simple atom*,' and that of a compound was called a '*compound atom*'. A 'compound atom' was formed by the union of atoms of different elements in simple proportions.

Limitations of Dalton's Theory.—Though *each kind ofatom has a definite weight*, the theory provided no means of determining even the relative weights of atom. Dalton asserted that *the combining weight of an element was its atomic weight*. But the correct relation between combining weight and atomic weight is :

atomic weight = equivalent weight × valency.

The atomic theory and the stoichiometric laws.—The laws of chemical combination by weight were all explained by the atomic theory—it being the *only* piece of evidence for the theory when it was proposed.

(i) **Law of conservation of mass.**—The weight of a chemical system is the sum of the weights of all the atoms in it. Chemical change involves merely a re-arrangement of atoms whose mass is constant and which remains unaltered during any chemical process. Hence no change of mass results in the re-grouping of atoms in a chemical reaction. That is, the weight of the system remains *constant*.

(ii) **Law of definite proportions.**—According to the atomic theory a compound is formed by the union of atoms in a simple fixed ratio.

Let *x* atoms of an element A unite with *y* atoms of another element B to form the molecule of a compound A*x*B*y*. Let the atomic weights of the elements A and B be *a* and *b* parts by weight respectively. According to Dalton's atomic theory, the atomic weight of an element is constant and hence the atomic weights *a* and *b* are constant ; and also the ratio *x* to *y* is fixed for the compound *A*xB*y*. Hence in all samples of A*x*B*y*, the ratio

$$\frac{\text{weight of A}}{\text{weight of B}}=\frac{x\times\text{atomic weight of A}}{y\times\text{atomic weight of B}}=\frac{x\times a}{y\times b}=\text{constant.}$$

That is, the compound A*x*B*y* has a constant composition. Hence the deduction of the law of definite proportions.

(iii) **Law of multiple proportions.**—Let the two elements A (at. wt. a) and B (at. wt. b) combine to form the compounds A*x*B*y*, AmBn, and ApBq in the simple ratio of atoms, *x*:*y*, *m*:*n* and *p*:*q* respectively. The proportions by weight of A and B in these compounds are :

Compound	Proportion by weight of A and B.
Ax By	ax : by or a : by/x
Am Bn	am : bn or a : bn/m
Ap Bq	ap : bq or a : bq/p

Let by/x = d, bn/m = e, bq/p = f.

The different weights of B combining with a fixed weight, namely *a* parts by weight of A are d, e and f ; their rato is :

d:e:f = by/x:bn/m:bq/p = ymp:xnp:qxm.

Now, since x, y, m, n, p and q are small integers, their products are also small whole numbers. Therefore, the ratio ymp:xnp:qxm is a ratio of small whole numbers and hence the law is deduced.

Taking the hydrocarbons acetylene C_2H_2, ethylene C_2H_4 and methane CH_4 for AxBy. AmBn and ApBq respectively, x=2, y=2, m=2, n=4, p=1, q=4, and the ratio ymp : nxp : qxm = 1 : 2 : 4.

(iv) **Law of reciprocal proportions.**—Consider the elements A, B and C, their atomic weights being *a*, *b*, and *c* units respectively. Let A separately combine with B and C to form A*x*B*y* and *A*m*C*n in simple ratio of atoms, *x*:*y* and *m*:*n*, respectively ; let *p* atoms of B combine with *q* atoms of C to form B*p*C*q*. The proportions by weight of A, B and C in these compounds are :

Compound	Proportion by weight
Ax By	ax : by or a : by/x
Am Cn	am : cn or a : cn/m
Bp.Cq	bp : cq

Let *by*/*x*=*d* and *cn*/*m*=*e*. The weights of B and C combining with a definite weight, namely *a* parts by weight of A are *d* and *e*. According to the law of equivalent proportions B and C should combine in the ratio of *d:e* or in simple multiple of this ratio. In *BpCq* B and C combine in the ratio of *bp:cq* by weight. Therefore,

bp:cq should be equal or simply related to *d:e*.

Now, d : c = by/x : cn/m = bym : cxn,

also $\frac{\text{bp}}{\text{cq}} = \frac{\text{bp} \times \text{ymxn}}{\text{cq} \times \text{ymxn}} = \frac{\text{bym} \times \text{pxn}}{\text{cxn} \times \text{qym}} = \frac{\text{d} \times \text{pxn}}{\text{e} \times \text{qym}}$

Since x, y, m, n, p and q are small whole numbers. Therefore bp/cq is either equal to d/e (when pxn = qym) or simply related to it, since pxn is a whole number, and so also qym, and hence the law.

Taking CH_4, CO_2 and H_2O for *AxBy*, AmCn and BpCq respectively, $x=1, y=4$, m=1, n=2, p=2 and q=1. ∴ pxn=4 and qym=4. That is bp/cq is equal to d/e.

The law of gaseous volumes.—*Under the same conditions of temperature and pressure the volumes of gases entering into a chemical reaction bear a simple ratio to one another and also to the product, if gaseous.*

This law was stated by the French scientist Gay Lussac in 1808.

Experiments show that under the same conditions of temperature and pressure :

(i) One volume of hydrogen combines with one volume of chlorine to form two volumes of hydrogen chloride ; and hence the ratio of their volumes is 1:1:2.

(ii) 2 volumes of hydrogen combine with one volume of oxygen to form two volumes of steam. Therefore, the required ratio is 2:1:2.

(iii) 1 volume of nitrogen combines with 3 volumes of hydrogen to yield 2 volumes of ammonia ; consequently, the ratio is 1:3:2.

Gay Lussac's law of gaseous volumes is, therefore, a generalisation of experimental results.

Adoption of Avogadro's hypothesis.—Dalton's atomic theory *assumes* that : *Elements combine in simple ratio by atoms ;* while Gay Lussac's law of gaseous volumes, *experimentally arrived at*, asserts that : *Gases combine in simple ratio by volume.* Consequently for chemical reaction between gases, there must be some simple relation between the volume of gases and the number of atoms contained in them.

The Swedish chemist, Berzelius, correlated the Gay Lussac's law and Dalton's atomic theory in the hypothesis :

Equal volumes of all gases at the same temperature and pressure contain the same number of atoms.

The term *atom* included Dalton's '*compound atoms*'.

But when applied to interpret experimental facts, Berzelius's hypothesis led to a conclusion which was in direct conflict with the fundamental assumption of Dalton's atomic theory *that atoms are indivisible.* Thus, it is found by experiments that one volume of hydrogen unites with one volume of chlorine to form 2 volumes of hydrogen chloride.

Let n represent the number of atoms present in one volume of hydrogen. Then, by Berzelius's hypothesis, n atoms of chlorine are also present in one volume of chlorine, and $2n$ *'compound atoms'* of hydrogen chloride are present in two volumes of it. Hence,

n atoms of hydrogen unite with n atoms of chlorine to give $2n$ 'compound atoms' of hydrogen chloride.

$\therefore$ 1 atom of hydrogen unites with 1 atom of chlorine to give 2 'compound atoms' of hydrogen chloride.

or $\frac{1}{2}$ atom of hydrogen unites with $\frac{1}{2}$ atom of chlorine to give 1 'compound atom' of hydrogen chloride.

The result goes against the atomic theory, since atoms, according to Dalton's atomic theory, are indivisible. Berzelius's hypothesis was therefore, vigorously disputed by Dalton. There was utter confusion for some time in the realm of chemistry, and the hypothesis was ultimately rejected. Dalton's atomic theory could not be reconciled with Gay Lussac's law, since the former made no distinction between the ultimate particles of elements and compounds. The difficulty was, however, overcome in a surprisingly simple way by the Italian scientist Amadeo Avogadro in 1811.

Gay Lussac's law and Dalton's atomic theory were correctly correlated by Avogadro who distinguished between two kinds of ultimate particles of matter, an atom and a molecule.

An atom is the smallest particle of an element which can take part in a chemical change.

A molecule is the smallest particle of an element or a compound which can exist in the free state.

Consequently the smallest unit of matter which can exist in a gas is not an atom but a molecule. So the volume of a gas is related to the number of molecules present in it. This is stated in Avogadro's hypothesis.

Avogadro's hypothesis.*—*Equal volumes of all gases under the same conditions of temperature and pressure contain the same number of molecules.*

The hypothesis correctly explains experimental facts. Thus it is found experimentally that :

1 volume of hydrogen unites with 1 volume of chlorine to give two volumes of hydrogen chloride.

Let n be the number of molecules present in 1 volume of hydrogen. Hence, by Avogadro's hypothesis :

n molecules of hydrogen unite with n molecules of chlorine to give $2n$ molecules of hydrogen chloride.

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* Also called Avogadro's law, since the hypothesis conforms to experimental tests of deductions made from it.

or 1 molecule of hydrogen unites with one molecule of chlorine to give 2 molecules of hydrogen chloride.

or 1 molecule of hydrogen chloride is obtained from $\frac{1}{2}$ molecule of hydrogen and $\frac{1}{2}$ molecule of chlorine.

This is not against the atomic theory, since molecules are not indivisible. The molecule can be split up into it constituent atoms. The Avogadro's hypothesis was, therefore, adopted.

Avogardro's hypothesis was found to fit in with Gay Lussac's law in perfect harmony with Dalton's Atomic Theory.

Avogadro's hypothesis and Dalton's Atomic Theory.—The adoption of Avogadro's hypothesis revolutionised our concept about the constitution of matter, and consequently substantially modified the atomic theory of Dalton. The modifications were mostly in the following lines : The concept of *simple atom* and *compound atom* was rejected—two kinds of smallest particle of matter recognised instead ; these are an *atom* and a *molecule*.

An atom, as stated already, is the smallest particle of an element which can take part in a chemical change ; the atom cannot usually exist as such in the *free state*.

A molecule, on the other hand, is the smallest particle of a substance (an element or a compound) which can exist in the *free state*. The properties of a substance are the properties of its molecules. Since atoms alone take part in a chemical change, prior to any chemical reaction, molecules of reacting substances first separate into atoms which then combine in simple numerical proportions to form molecules of new substances.

Applications of Avogadro's hypothesis.—The hypothesis not only explained Gay Lussac's law of gaseous volumes, but also greatly extended the usefulness of Dalton's atomic theory by clearly explaining the confusion arising out of the concept of 'simple atom' and 'compound atom'.

The hypothesis is perfectly general in its applications, but it was only some fifty years later after its adoption that Cannizzaro, a pupil and a countryman of Avogadro, successfully applied it to experimental results in the year 1858. The hypothesis affords methods :

(*i*) *to determine the number of atoms in the molecules of a gaseous element*, i.e., *its atomicity*.

(*ii*) *to compare the molecular weights of gases and vapours and to deduce that the molecular weight of any gas or vapour is twice its vapour density*.

(*iii*) *to establish that the gram-molecular weight of any gas or vapour occupies 22.4 litres at N.T.P.*

(*iv*) *to deduce the molecular formula of a compound from its volumetric composition*.

(*v*) *to determine the atomic weight of an element*.

(i) To determine the number of atoms in the molecule of a gaseous element, i.e., its atomicity.

(a) Experiment shows that :

1 volume of hydrogen combines with 1 volume of chlorine to form 2 volumes of hydrogen chloride.

Let 1 volume of hydrogen contain n molecules of it, then, by Avogadro's hypothesis :

n molecules of hydrogen + n molecules of chlorine
= $2n$ molecules of hydrogen chloride.

or 1 molecule of hydrogen + 1 molecule of chlorine
= 2 molecules of hydrogen chloride.

or $\frac{1}{2}$ molecule of hydrogen + $\frac{1}{2}$ molecule of chlorine
= 1 molecule of hydrogen chloride.

But according to Dalton's atomic theory, each molecule of hydrogen chloride being a compound of hydrogen and chlorine, must contain *at least* one atom each of hydrogen and chlorine—coming from $\frac{1}{2}$ molecule each of hydrogen and chlorine. Hence *a molecule of hydrogen or chlorine must contain at least* 2 *atoms, since atoms are indivisible.*

The exact number of atoms in a hydrogen molecule can be ascertained as follows :

(i) The number of different sodium salts that an acid can yield is a measure of its replaceable hydrogen atoms. Thus, sulphuric acid, H_2SO_4, yields two sodium salts, $NaHSO_4$, and Na_2SO_4, the two hydrogen atoms of the acid being replaceable in two stages. In a similar manner by replacing 3 hydrogen atoms of phosphoric acid, H_3PO_4 in three stages, three sodium salts, NaH_2PO_4, Na_2HPO_4 and Na_3PO_4 can be obtained. Hence the number of sodium salts that an acid forms is equal to its number of replaceable hydrogen atoms. Now hydrochloric acid yields only *one* sodium salt. The hydrochloric acid molecule, therefore, contains only one atom of hydrogen. But it has been shown to contain, as above, half a molecule of hydrogen. Half a molecule of the gas, therefore, contains one atom of hydrogen. Hence a molecule of hydrogen, contains two atoms, or in other words, *the hydrogen molecule is diatomic,* i.e., *the atomicity of hydrogen is two.*

(ii) The ratio of the specific heat of a gas at constant pressure, Cp, and that at constant volume, Cv, has been found to be equal to 1.44, i.e., $Cp/Cv = 1.44$, for diatomic gases. In the case of hydrogen this ratio is found to be 1.44, and hence the gas is diatomic.

(b) 2 vols. of hydrogen + 1 vol. of oxygen = 2 vols. of steam.

Let 1 volume hydrogen contain n molecules of it, then by Avogadro's hypothesis :

2 molecules of hydrogen + 1 molecule of oxygen = 2 molecules of steam.

or 1 molecule of hydrogen + $\frac{1}{2}$ molecule of oxygen = 1 molecule of steam.

But 1 molecule of steam must contain *at least* one atom of oxygen, coming from $\frac{1}{2}$ molecule of oxygen. Hence *a molecule of oxygen is at least diatomic.*

The *atomicity*, i.e., the number of atoms in a molecule of elementary gases like hydrogen, oxygen, nitrogen, chlorine, etc., is *two* only.

(ii) **The molecular weight of any gas or vapour is twice its vapour density.**

The density of a gas or vapour relative to hydrogen is the ratio of the weight of a volume of the gas or vapour to the weight of the *same* volume of hydrogen under the same conditions of temperature and pressure.

By definition, *relative density* or *vapour density*, as it is called.

$$= \frac{\text{weight of a certain volume of the gas or vapour}}{\text{weight of the } \textit{same} \text{ volume of hydrogen}}$$

at the same temperature and pressure. But equal volumes of the gas and hydrogen contain the same number of molecules, say, n, by Avogadro's hypothesis. Hence,

$$\text{vapour density} = \frac{\text{weight of } n \text{ molecules of the gas or vapour}}{\text{weight of } n \text{ molecules of hydrogen}}$$

$$= \frac{n \times \text{weight of 1 molecule of the gas or vapour}}{n \times \text{weight of 1 molecule of hydrogen}}$$

$$= \frac{\text{mol. wt. of gas or vapour}}{\text{mol. wt. of hydrogen}}$$

$$= \frac{\text{mol. wt. of gas or vapour}}{2}$$

since the atomic weight of hydrogen is taken as 1 and its mol. wt. is 2—the hydrogen molecule H_2 being diatomic.

$\therefore$ mol. wt. of gas or vapour $= 2 \times$ vapour density.

Actually the atomic weight of hydrogen is 1.008 and its molecular weight is 2.016 instead of 2, so that

$$\textit{molecular weight} = \textit{vapour density} \times 2.016.$$

(iii) **Gram-molecular weight of any gas or vapour occupies 22.4 litres at N.T.P.**

Molecular weight of any gas or vapour expressed in grams is its gram molecular weight. One litre of hydrogen at N.T.P. weighs 0.09 gm. nearly. Density of gas or vapour (H = 1)

$$= \frac{\text{weight of 1 litre of the gas or vapour at N.T.P.}}{\text{weight of 1 litre of hydrogen at N.T.P.}}$$

$$= \frac{\text{weight of 1 litre of the gas or vapour at N.T.P.}}{0.09}$$

$\therefore$ weight of 1 litre of a gas or vapour at N.T.P.

$= 0.09 \times$ its vapour density $= 0.09 \times (M/2.016)$.

where M = gram-molecular weight of the gas.

i.e., $0.09 \times (M/2.016)$ gm. of a gas or vapour occupy a volume of 1 litre at N.T.P.

$\therefore$ M gm. of any gas or vapour occupy (2.016/0.09) or 22.4 litres at N.T.P.

Hence, the gram-molecular weight of *any* gas or vapour occupies 22.4 litres at N.T.P. This is called the *gram-molecular volume or molar volume.*

(iv) Molecular formula of a compound from its volumetric composition.

Experiments show that : 2 volumes of steam are obtained from 2 volumes of hydrogen and 1 volume of oxygen.

Suppose 1 volume of steam contains n molecules of it, then, by Avogadro's hypothesis, $2n$ molecules of steam are obtained from $2n$ molecules of hydrogen and n molecules of oxygen.

$\therefore$ 2 molecules of steam are obtained from 2 molecules of hydrogen and 1 molecule of oxygen.

$\therefore$ 1 molecule of steam is obtained from 1 molecule of hydrogen and half molecule of oxygen.

Now, 1 molecule of hydrogen contains 2 atoms of hydrogen ; half-molecule of oxygen contains 1 atom of oxygen.

$\therefore$ the simple formula for steam is H_2O.

Again, the molecular weight of steam $= 2 \times 9 = 18$; 9 is the vapour density of steam determined experimentally.

Hence, the formula H_2O for steam is confirmed, since 1 molecule of steam can contain only 1 atom of oxygen, its atomic weight being 16.

(v) Atomic weight of an element.—(a) From the atomicity of elementary gases :

Atomic weight = molecular weight ÷ atomicity.

Molecular weight is deduced from the determination of vapour density. The molecular weight of the element argon, for example, is found to be 39.9 and its atomicity is 1. Hence the atomic weight of argon is 39.9.

(b) **Cannizzaro's method of least weight.**—Since an atom is indivisible, no molecule of a compound can contain less than one atom of any element. Hence, *the atomic weight of an element may be defined as the smallest weight of it found in the molecular weight of any of its compounds.*

The method depends upon the determinations of :

(i) the molecular weights of a large number of **volatile** compounds (deduced from the relation molecular weight $= 2 \times$ vapour density, vapour density being determined experimentally).

(ii) their percentage composition by direct analysis. The weight of the element present in the molecular weight of each compound is then calculated—the least of these weights is the *probable* atomic weight of the element.

The method is obviously applicable in the case of elements which form a large number of *volatile* compounds. The application of the method to nitrogen is illustrated below.

Compound	Mol. wt.	% N_2 by wt.	Wt. of N_2 per mol.
Ammonia	17	82.3	$17 \times 0.823 = 14$
Nitrous oxide	44	63.6	$44 \times 0.636 = 28$
Nitric oxide	30	46.6	$30 \times 0.466 = 14$
Dinitrogen tetroxide	92	30.4	$92 \times 0.304 = 28$

Hence, the *probable* atomic weight of nitrogen is 14, since it is the least weight of nitrogen found in any of its compounds.

Molecular weights determined from vapour densities of the compounds are not exact, and consequently the atomic weights found by Cannizzaro's method are only approximate.

Exercises

1. A metal is found to give two oxides ; on heating 1 gm. of each in a current of hydrogen, 0.798 and 0.888 gms. of the metal were obtained. Show that the results are in agreement with the law of multiple proportion. *Cal.* '31 ; *Banaras,* 1937.

In the first oxide (1−0.798) or 0.202 gm. of oxygen unite with 0.798 gm. of the metal.

∴ 1 gm. of oxygen unites with 0.798/0.202 or 3.95 gms. of the metal.

In the second oxide (1−0.888) or 0.112 gm. of oxygen unites with 0.888 gm. of the metal.

∴ 1 gm. of oxygen unites with 0.888/0.112 or 7.9 gm. of the metal.

Hence the weights of the metal uniting with a constant weight, namely, 1 gm. of oxygen, are as 3.95 to 7.9, that is, as 1 : 2. Hence the agreement:

2. Illustrate the law of reciprocal proportions from the composition of the following compounds :

Marsh gas :- 75% carbon, 25% hydrogen ; carbon monoxide :- 42.86% carbon, 57.14% oxygen ; and water :- 11.11% hydrogen, 88.89% oxygen. *Nagpur,* 1935.

In marsh gas 1 gm. of carbon unites with 25/75 or 0.33 gm. of hydrogen ;

In carbon monoxide 1 gm. of carbon unites with 57.14/42.86 or 1.33 gm. of oxygen.

Hence, hydrogen and oxygen should unite in the ratio of 0.33 to 1.33, i.e., in the ratio of 1 to 4 ; or in some simple multiples thereof.

In water 11.11 gm. hydrogen unite with 88.89 gm. of oxygen.

∴ 1 gm. of hydrogen unites with 88.89/11.11 or 8 gms. of oxygen.
i.e., hydrogen and oxygen unite to form water in the ratio of 1 to 8 parts by weight, that is, in the ratio of 1 to 2×4 parts by weight.

Hence these figures agree with the law of reciprocal proportions.

3. Two oxides of a metal M. when heated to a constant weight in a current of hydrogen give 0.12585 g. and 0.2264 g. of water respectively per gram of the oxides used. If the formula for the latter be given by MO, find that for the other. *Calcutta,* 1951.

18 gms. of water H_2O contain 16 gms. of oxygen.

∴ 0.12585 g. of water contains $\frac{16}{18} \times 0.12585 = 0.1119$ gm. of oxygen.

This 0.1119 g. of O_2 comes from 1 gm. of first oxide, and hence in 1 gm. of first oxide, M = 0.8881 gm., and O = 0.1119 gm.

0.2264 gm. of water contain $\frac{16}{18} \times 0.2264 = 0.2013$ gm. of oxygen.

∴ in 1 gm. of second oxide, M = 0.7987 gm., and O = 0.2013 gm.

Now, formula of the second oxide is MO, i.e.,

$$\frac{\text{Number of atoms of M}}{\text{Number of atoms of O}} = \frac{1}{1} = \frac{0.7987/x}{0.2013/16},$$

where x = atomic weight of M, and 16 = atomic weight of oxygen.

$$\therefore \quad x = \frac{0.7987}{0.2013} \times 16 = 63.49.$$

In the first oxide, $\frac{\text{number of atoms of M}}{\text{number of atoms of O}} = \frac{0.8881/63.49}{0.1119/16} = \frac{2}{1}$

∴ formula of first oxide is M_2O.

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4. State and explain the laws of chemical combination. Give some account of experimental evidence upon which they are based.

Two oxides *a* and *b* of a certain metal were heated to constant weight in a current of hydrogen and the water obtained in each case was weighed. The following results were obtained : 2 gm. of *a* gave 0.2517 gm. of water, and 1 gm. of *b* gave 0.2264 gm. of water. Show that the above results illustrate the law of multiple proportion.

5. Illustrate the law of equivalent proportion from the following analysis :

Potassium chloride	:	potassium	52.5% ;	chlorine	47.5%.
Potassium iodide	:	potassium	23.6% ;	iodine	76.4%.
Chloride of iodine	:	iodine	78.2% ;	chlorine	21.8%.

6. What is Avogadro's hypothesis ? Explain, with illustrations, how this hypothesis brings into harmony Dalton's atomic theory and Gay Lussac's law of combining volumes. State how it is used to prove that (i) the atomicity of oxygen is two ; (ii) the molecular weight of any gas is twice its vapour density, and (iii) the gram molecular weight of any gas is 22.4 litres at N.T.P. *Dacca Inter.*

7. State and explain Gay Lussac's Law of combining volumes. Four compounds of an element contain respectively 42.8%, 27.3%, 80%, and 64.90% of the element. The weights of one litre of each of these compounds in a gaseous state at N.T.P. are 1.26 gms., 1.98 gms., 1.35 gms. and 3.33 gms. respectively. Calculate the probable atomic weight of the element. *Ans.* 12.

8. State how the results given below illustrate a law of chemical action. Enunciate the law.

(a) 0.46 gm. of magnesium produces 0.77 gm. of magnesium oxide.

(b) 0.82 gm. of magnesium liberates 760 c.c. of hydrogen at N.T.P. from an acid.

(c) 1.26 gm. of water result from the union of 1.12 gm. of oxygen with hydrogen.

9. State and explain the law of multiple proportions. Two oxides of an element are found to contain 36.84 and 46.67 per cent of the element respectively. Show that these figures illustrate the law of multiple proportion. *P. U.* '61.

10. State Dalton's Atomic Theory and show how the laws of chemical combination can be deduced from it. *Inter. Science, Lonodon.*

11. The percentage composition of ferrous sulphide is : iron 63.53 per cent., sulphur 36.47 per cent. Two grams of iron are heated with 5 gms. of sulphur. How much ferrous sulphide is formed and how much sulphur remains uncombined ?
Ans. 3.148 gms. ; 3.852 gms.

12. State and illustrate the law of multiple proportions. Explain how it follows directly from Dalton's atomic theory. *Gauhati*, 1952.

Two oxides of a metal contain 27.6 and 30.0 per cent of oxygen respectively. If the formula of the first be M_3O_4, find that of the second. *Cal.* 1940 ; *Ans.* M_2O_3.

13. Enunciate Avogadro's hypothesis. Discuss how the hypothesis has proved useful in the determination of atomic weights of gaseous elements. *Cal.* 1957 ; 1959.

VIII

EQUIVALENT WEIGHT, ATOMIC WEIGHT AND MOLECULAR WEIGHT

An important consequence of the law of reciprocal proportions is the emergence of the idea of equivalent weight ; thus :

In *sodium hydride*, NaH, the ratio by weight of hydrogen to sodium is 1 : 23.

In *hydrogen chloride*, HCl, the ratio by weight of hydrogen to chlorine is 1 : 35.457.

The law of reciprocal proportions suggests that sodium and chlorine will combine in the proportion of 23 : 35.457 or in a simple multiple of this proportion. Thus, 23 parts by weight of sodium combine with 35.457 parts by weight of chlorine to form sodium chloride. 23 and 35.457 are the *equivalent weights* of sodium and chlorine respectively. Hence :

Elements combine in the ratio of their equivalent weights or their multiples.

Standard of Equivalents.—In finding out the equivalent weight of an element it is necessary to fix upon a standard of reference—this is taken as 8 parts by weight of oxygen i.e., *equivalent weight of oxygen is always* 8.000 *by definition.*

Equivalent weight.—*The equivalent weight of an element is defined as the number of parts by weight of that element which will combine chemically with or will replace from chemical combination*, 8.000 *parts by weight of oxygen, or its equivalent, such as* 1.008 *parts by weight of hydrogen or* 35.457 *parts by weight of chlorine.*

The equivalent weight is a *number ; the gram equivalent is the equivalent weight expressed in grams.* The equivalent weight is an experimental quantity.

Illustrations.—(i) 1.008 parts by weight of hydrogen combine with 8 parts by weight of oxygen to form water, H_2O ; the equivalent weight of hydrogen, therefore, is 1.008.

(ii) 1.008 parts by weight of hydrogen combine with 35.457 parts by weight of chlorine to form hydrogen chloride, consequently the equivalent weight of chlorine is 35.457.

(iii) 35.457 parts by weight of chlorine combine with 107.88 parts by weight of silver ; equivalent weight of silver is, therefore, 107.88.

(iv) 12.16 parts by weight of magnesium displace 1.008 parts by weight of hydrogen from dilute sulphuric acid. 12.16 is the equivalent weight of magnesium :

$$Mg + H_2SO_4 = MgSO_4 + H_2.$$

Equivalent weight may vary.—Equivalent weight of an element is determined by direct analysis of its compounds. When it forms more than one compound with another element, its equivalent naturally varies. Thus, iron forms two oxides : ferrous oxide, FeO ; ferric oxide, Fe_2O_3.

Compound	Composition by weight	Equivalent weight
Ferrous oxide	Fe : O = 27.925 : 8	Fe = 27.925
Ferric oxide	Fe : O = 18.616 : 8	Fe = 18.616
Carbon dioxide	C : O = 3.00 : 8	C = 3.00
Carbon monoxide	C : O = 6.00 : 8	C = 6.00

Also, *atomic weight = equivalent weight × valency.* Valency of many elements is variable, so also their equivalent weight, since the atomic weight is constant.

Determination of equivalent weights of metals.—(i) By displacing hydrogen from an acid by a given weight of the metal.

When a metal displaces hydrogen from an acid, the displacement takes place in equivalent amounts. The hydrogen liberated is collected, its volume measured in c.c. and reduced to N.T.P., and its weight calculated from the ralation :

Weight of hydrogen = c.c.'s of hydrogen at N.T.P. × 0.00009 gm., since weight of 1 c.c. of hydrogen at N.T.P. = 0.00009 gm.

$$\text{Equivalent weight of the metal} = \frac{\text{Weight of the metal} \times 1.008.}{\text{Weight of hydrogen liberated.}}$$

The method is limited in its applicability to metals which dissolve in dilute acids (or alkali) with evolution of hydrogen. *Calcium, magnesium, zinc and iron* dissolve in cold dilute HCl or H_2SO_4, evolving hydrogen. Aluminium dissolves in fairly strong HCl or warm alkali, while tin dissolves only in hot and strong hydrochloric acid The method has been used to determine equivalents of zinc and *aluminium*.

Equivalent weight of zinc.—About 0.1 gm. of zinc is accurately weighed out in a watch glass, which is then placed in a beaker—the zinc being covered with a funnel. Water is then added till the stem of the funnel is under water. A graduated tube completely filled with water is inverted over the funnel and fairly strong sulphuric acid is added to the beaker. Quick evolution of hydrogen takes place on the addition of few drops of copper sulphate solution—the gas collects in the tube. When the zinc completely dissolves, the tube is taken out by closing the open end with the thumb, and placed in a jar of water so that the level of water inside and outside becomes the same. The volume of hydrogen is noted, so also the barometric pressure at the time and the temperature of water. (fig. 33).

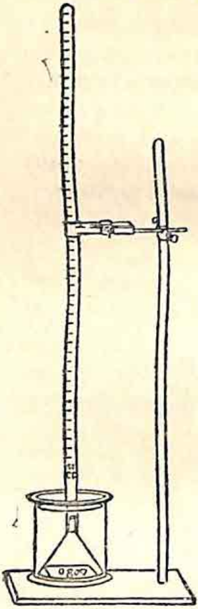

Fig. 33

$$Zn + H_2SO_4 = ZnSO_4 + H_2$$

Calculation :

Let the weight of zinc = w gm.
Volume of hydrogen collected = v c.c.
Temperature of water = t° C.
Barometric pressure = P mm.
Aqueous tension at t°C = f mm.

Barometric pressure = pressure of H_2 + aqueous tension at t°C.

$\therefore$ Pressure of $H_2 = (P-f)$ mm.

Let the volume of the hydrogen at N.T.P. be v′ c.c.

$$\therefore \frac{v.(P-f)}{(273+t)} = \frac{v'.760}{273}, \quad \text{or } v' = \frac{v \times (P-f) \times 273}{(273+t) \times 760} \text{ c.c.}$$

Now, 1 c.c. of hydrogen at N.T.P. weighs 0.00009 gm. nearly.

∴ v′ c.cs. of hydrogen at N.T.P. weigh v′×0.00009 gm.

$$\therefore \text{ equivalent of zinc} = \frac{w\times 1.008}{v'\times 0.00009} = \frac{w\times(273+t)\times 760\times 1.008}{v\times(P-f)\times 273\times 0.00009}$$

(ii) **By converting a known weight of the metal into its oxide, and weighing the oxide.**

Equivalent weight of copper.—A porcelain crucible with its lid is weighed. A few pieces of clean copper foil, about 2 gm., are put into the crucible, which is again weighed with its lid. Few drops of moderately strong nitric acid are added to the copper foils in the crucible—a vigorous reaction takes place with the evolution of brown fumes. When the copper has dissolved fully, the solution is carefully evaporated to dryness on a hot asbestos plate so that none of the green copper nitrate is lost by spirting. The crucible with its lid placed slightly on its side is then heated on a clay-pipe triangle when the green copper nitrate is converted into the black copper oxide, and more brown fumes are evolved. When the reaction has ceased, the crucible with its lid is allowed to cool in a desiccator and weighed again. The process of heating, cooling and weighing is repeated till the final weight is constant. The weight of copper combining with 8 gm. of oxygen is found out by proportion.

$$Cu+4HNO_3 = Cu(NO_3)_2+2H_2O+2NO_2$$
$$2Cu(NO_3)_2 = 2CuO+4NO_2+O_2$$

Calculation :

	gm.
Weight of crucible+lid	a
Weight of crucible+lid+copper	b
Weight of crucible+lid+copper oxide	c
∴ weight of copper	(b−a)
Weight of copper oxide	(c−a)
∴ weight of oxygen	(c−b)

$$\therefore \text{ equivalent weight of copper} = \frac{(b-a)}{(c-b)}\times 8.$$

Tin reacts with strong nitric acid to give hydrated stannic oxide directly without the formation of any nitrate at all.

(iii) **By the analysis of halides.—Equivalent weight of sodium.** A weighed quantity of pure sodium chloride is dissolved in distilled water containing a little nitric acid, and precipitated as silver chloride by adding an excess of silver nitrate solution. The curdy white precipitate of the silver chloride is filtered, washed, dried and weighed. The reaction is :

$$NaCl+AgNO_3 = AgCl+NaNO_3.$$

One equivalent of sodium chloride produces one equivalent of silver chloride. Hence the equivalent weight of sodium chloride is the weight which produces 143.34 gm. of silver chloride. 143.34 gm. is equal to 1 gram-equivalent of silver chloride, i.e., 107.88 gm. of silver react with 35.46 gm. of chlorine to form (107.88+35.46) = 143.34 gm. of AgCl.

The equivalent of sodium is 35.457 less than the equivalent of sodium chloride, since sodium and chlorine have combined in equivalent amounts.

Calculation.—Let the weight of sodium chloride = w gms.

The weight of silver chloride = w′ gms.

w′ gms. of AgCl are produced by w gm. of the sodium chloride.

∴ 143.34 gms. of AgCl are produced by 143.34 w/w′ gm. sodium chloride.
i.e., equivalent of sodium chloride = 143.34 w/w′.

∴ the equivalent weight of sodium = (143.34 w/w′) − 35.457.

Alternatively, let the equivalent of sodium = x.

∴ the equivalent of sodium chloride = $x+35.457$.

$$\frac{\text{Equivalent of sodium chloride}}{\text{Equivalent of silver chloride}}=\frac{\text{weight of sodium chloride}}{\text{weight of silver chloride.}}$$

i.e., $(x+35.457)/143.34 = w/w'$, ∴ $x = (143.34\ w/w') - 35.357$.

The method has been used in determining the equivalents of *sodium, potassium, calcium, magnesium*, etc.

(iv) **By the replacement of metals.**—A more electropositive metal displaces a less electropositive metal from its salts in solution—*the displacement taking place in equivalent amounts.* The method is applicable when a metal displaces another from a solution. Thus if iron powder is added to copper sulphate solution, a red deposit of copper is formed and iron dissolves.

$$CuSO_4+Fe = FeSO_4+Cu.$$

$$\frac{\text{Eq. wt. of Cu}}{\text{Eq. wt. of Fe}}=\frac{\text{wt. of Cu deposited}}{\text{wt. of Fe dissolved}}$$

Knowing the equivalent weight of copper, that of iron can be found out, or *vice versa.*

(v) **From electro-chemical equivalents.**—The equivalent weight may be determined from the relation (*vide electrolysis*) :

$$\text{Equivalent weight} = \frac{\text{electro-chemical equivalent}}{0.0000104}\times 1.008.$$

Atomic weight.—Each kind of atom has a definite *weight.* But as mentioned before, it is difficult to determine the absolute weight of an atom of the element (p. 16). It has been convenient in practice to state the relative weight of any atom in terms of that of a standard atom.

Fromerly the atom of the lightest element hydrogen was chosen (by Dalton) as the standard of comparison and its atomic weight was taken as unity. But now the standard of comparison is oxygen.

Since atomic weight is generally determined from the equvailent weight, 16.00 is taken as the atomic weight of oxygen.

The atomic weight of an element is the weight of an atom of the element relative to the weight of the oxygen atom taken as 16.0000. On this basis, the atomic weight of hydrogen is 1.008.

Relation between atomic weight and equivalent weight—Let

the atomic weight of the element $= a$
equivalent weight of the element $= e$
valency of the element $= v$

then, by definition of valency :

v atoms of hydrogen combine with 1 atom of the element,

or, v parts by weight of hydrogen combine with a parts by weight of the element,

or 1 part by weight of hydrogen combines with a/v parts by weight of the element.

Hence, by definition of equivalent weight, $a/v = e$, or $a = e \times v$, i.e., *atomic weight = equivalent weight × valency*.

Determination of atomic weights.—The exact atomic weight of an element is determined from the relation :

atomic weight = equivalent weight × valency.

The atomic weight of an element is, therefore, either the same as the equivalent weight when the valency is 1, or an exact multiple of the equivalent weight, since the valency is always a small integer. The determination of atomic weight resolves into two parts.

(a) *the determination of the equivalent weight.* This may be accurately found out by chemical analysis.

(b) *the determination of the valency of the element.* The valency is usually determined by dividing the approximate atomic weight (which may be found out in several ways, as mentioned below) by the equivalent weight and taking the nearest integer as a correct number, since the valency is always a whole number.

The approximate atomic weight may be found out in several ways :

(i) **By Dulong and Petit's law :**—The atomic heat of a solid element (except *carbon*, *silicon*, *boron*, *and beryllium*) is approximately constant at ordinary temperature, and is equal to 6.3 nearly. Dulong and Petit put forward the above law in 1819.

The product of the atomic weight and specific heat of an element is known as atomic heat, and consequently,

atomic weight × specific heat = 6.3 approximately.

The law is *approximate* and applies to *solid* elements only.

In order to determine the exact atomic weight find out :

(a) approximate atomic weight from the relation :

approximate at. wt. = 6.3/sp. ht. ;

(b) then valency from : valency = approximate at. wt./eq. wt.

The valency, thus obtained, is corrected to the nearest integer, since valency is always a whole number.

(c) *finally*, apply the relation exact at. wt. = eq. wt. × valency.

Example.—*0.5574 gm. of a metal was converted into* 0.6817 gm. of *oxide. The specific heat of the metal is* 0.063. *Find the exact atomic weight.*

The equivalent of metal $= \frac{0.5574}{0.1243} \times 8 = 35.88$

By Dulong and Petit's law (atomic weight × specific heat = 6.3 nearly)

rough atomic weight $= 6.3/0.063 = 100$.

$\therefore$ valency $= \frac{\text{rough atomic weight}}{\text{equivalent weight}} = \frac{100}{35{\cdot}88} = 2.8$.

Hence valency is taken as 3, since valency is always an integer.

$\therefore$ exact atomic weight $= 35.88 \times 3 = 107.64$.

(ii) **By Cannizzaro's method :**—*From molecular weights of volatile compounds.*—The method gives the *probable atomic* weight. The weight is approximate only. (see page 70).

(iii) **By finding the vapour density (and hence the molecular weight) of a volatile salt,** usually a chloride, of the element.

Let x and E be the valency and equivalent of the element, M.

Then, Ex=atomic weight of the element.

Let $MClx$ be the formula of the chloride.

$\therefore$ molecular weight of the chloride $= Ex + 35.46x$.

$$x = \frac{\text{Mol. wt. of chloride}}{E+35.46} = \frac{2 \times \text{vapour density}}{E+35.46}$$

Example.—*The vapour density of boron chloride is* 59. *The equivalent of boron is* 3.607. *Find the atomic weight of boron.*

Let the valency of the element be x and the formula of the chloride BClx. The atomic weight of B is 3.607.x The molecular weight of the chloride is (3.607x+35.46) and is equal to 2×59.

$\therefore$ $3.607x + 35.46x = 2 \times 59$, whence $x = 3.02 = 3$ (to nearest integer),

$\therefore$ the atomic weight $= 3.607 \times 3 = 10.82$.

(iv) **By Mitscherlich's law of isomorphism** (1820).—Substances are said to be isomorphous when they have the same crystalline structure. Thus, zinc sulphate $ZnSO_4,7H_2O$, and ferrous sulphate $FeSO_4,7H_2O$ are isomorphous, so also potash alum, $K_2SO_4,Al_2(SO_4)_3,24H_2O$, and chrome alum K_2SO_4, $Cr_2(SO_4)_3$, $24H_2O$, potassium sulphate, K_2SO_4, and potassium chromate, K_2CrO_4 ; also the phosphate and arsenate of sodium, Na_3PO_4, $12H_2O$ and Na_3AsO_4, $12H_2O$.

Criteria of isomorphism.—(i) *Similarity of crystaline structure.*

(ii) *Formation of mixed crystals*—From a solution of isomorphous compounds (*potash a lum and chrome alum,* for example) homogeneous crystals separate containing varying amounts of either substances.

(iii) *Formation of overgrowths*—A crystal of a substance is found to grow in size when suspended in a solution of an isomorphous compound—a crystal of chrome alum, for example, is covered with layers of potash alum when suspended in a solution of the latter.

The *valency* of two elements forming isomorphous compounds is the same. Hence knowning the valency of one element, that of the other is found out ; atomic weight is then found out from the relation :

Atomic weight = equivalent weight × valency.

Thus, ferric oxide is isomorphous with aluminium oxide Al_2O_3 in which aluminium trivalent ; formula for ferric oxide should be Fe_2O_3 with trivalent iron.

Molecular weight.—Molecular weight of a substance is the sum of the atomic weights of all the atoms contained in a molecule, and consequently the molecular weight of a substance is also a relative weight based on the same standard of comparison as is used for the atomic weight. *The molecular weight of a substance may*, therefore, *be defined as the weight of a molecule of the substance relative to the weight of the oxygen atom as* 16.0000.

Sulphuric acid, H_2SO_4, for example, contains 2 atoms of hydrogen, 1 atom of sulphur and 4 atoms of oxygen ; hence its molecular weight

$$= 2 \times 1.008 + 32.066 + 4 \times 16 = 98.082.$$

The molecular weight of a subsstance in grams is referred to as the **gram molecular weight** or the **gram molecule** or simply as a **mole.**

The gram-molecular weight of any gas or vapour occupies 22.4 litres at N.T.P. This is called **gram-molecular volume** or simply **molar volume.**

The atomic and molecular weights, as stated above, refer to relative weights only, but they are related to the absolute weights of the atoms and molecules. 1 gram atom or 1 gram molecule of a substance always contains a constant number of individual atoms or molecules—this constant, called **Avogadro number,** *is defined as the number of individual molecules in* 1 *gram molecule of a substance ;* its value is 6.023×10^{23}. The number of individual atoms in 1 gram atom is also equal to this number. The absolute weight of an atom or a molecule is obtained by dividing the atomic or molecular weight of a substance by the Avogadro number. Absolute weight of :

a hydrogen molecule $= 2.016/6.023 \times 10^{23} = 0.3347 \times 10^{-23}$ gm.

a hydrogen atom $= 1.008/6.023 \times 10^{23} = 0.1673 \times 10^{-23}$ gm.

The absolute weight of an atom = the atomic weight of the element multiplied by 0.1673×10^{-23} gm.

Thus the absolute weight of a carbon atom $= 12 \times 0.1673 \times 10^{-23}$ gm.

1 c.c. of hydrogen at N.T.P., weighing 0.00009 gm. contain about 3×10^{19} hydrogen atoms.

Exercises

1. 0.218 gm. of magnesium when dissolved in HCl, give 218.2 c.c. of hydrogen collected over water, at 17°C and 754.5 mm. pressure. Find the equivalent of magnesium. Aqueous tension at 17°C = 14.4 mm. *Patna*, 1928.

Volume of hydrogen = 218.2 c.c. ;

Its pressure = 754.5 − 14.4 = 740.1 mm. ;

Its temperature = 17°C = 273 + 17 = 290° abs.

Let the volume at N.T.P. = v c.c.

$$\therefore \frac{v \times 760}{273} = \frac{218.2 \times 740.1}{290}, \text{ whence } v = 200 \text{ c.c.}$$

Weight of 200 c.c. hydrogen at N.T.P. $= 200 \times 0.00009$ gm.

$$\therefore \text{ equivalent of magnesium} = \frac{0.218}{200 \times 0.00009} = 12.12.$$

2. The chloride of an element was converted quantitatively into the corresponding oxide and the following figures were obtained : 0.1827 gm. of the chloride gave 0.1057 gm. of the oxide. Calculate the equivalent of the element.
Cambridge University.

Let x be the equivalent ; then, $(x+35.5)$ gms. of the chloride give $(x+8)$ gms. of the oxide, where 35.5 and 8 are the equivalents of chlorine and oxygen respectively.

$$\therefore \quad \frac{x+8}{x+35.5}=\frac{0.1057}{0.1827}, \text{ whence } x = 29.74$$

3. The vapour density of the chloride of an element M is 66 and the oxide of the element contains 53% of the element. Calculate the valency and the probable atomic weight.
London University

47 gms. of oxygen unite with 53 gm. of the element.

$\therefore$ 8 gms. of oxygen unite with $53 \times 8/47$ or 9 gms. of the element.

$\therefore$ the equivalent of the element is 9.
Let the valency of the element be x.

$\therefore$ its atomic weight = valency × equivalent = $9x$.

Suppose the formula of the chloride is MCl_x.

$\therefore$ $9x + 35.5x = 132$ (mol. wt. $= 2 \times 66$) whence $x = 3$.

4. 0.1 g. of a metal of which the specific heat is 0.214, on solution in hydrochloric acid displaced 124.4 c.c. of dry hydrogen at N.T.P. Calculate the atomic weight of the metal.
Calcutta, '53.

Equivalent weight of the metal $= 0.1/124.4 \times 0.00009 = 8.933$

Rough atomic weight $= 6.3/0.214 = 29.44$

$\therefore$ valency = rough atomic weight/equivalent weight $= 29.44/8.933$
$= 3.296 = 3$, since valency is an integer.

$\therefore$ exact atomic weight $= 8.933 \times 3 = 26.80$.

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5. What is meant by the equivalent weight of an element and how is it related to its atomic weight ? Describe an experiment to determine the equivalent of copper.
Calcutta '42.

6. 10.788 g. of metallic silver (at. wt. 107.88) when heated in chlorine, yielded 14.3337 g. of silver chloride. Calculate the atomic weight of chlorine. 35.457.

7. 0.3697 g. of Al liberated 0.04106 g. of H_2 on being dissolved in a strong solution of sodium hydrate ; find the at. wt. of Al. 27.009.

8. 0.177 g. of a metal when dissolved in dilute hydrochloric acid evolved 177 c.c. of dry hydrogen gas at 12°C and 766 mm. Find the equivalent of the metal.
Calcutta '09. 11.5

9. 1.113 g. of Cu combine with 0.28 g. of O_2. Calculate the equivalent of copper.
Lond. Mat. 31.8.

10. Magnesium oxide contains 60% magnesium. What is its equivalent weight ? 12

11. 0.24 g. of a metal (at. wt. 24) displaces 224 c.c. of H_2 at N.T.P. from an acid. What is the valency of the metal ? 2

12. In an experiment 0.49 gm. of a metal when dissolved in HCl gave 295 c.c. of dry hydrogen at 22°C and 752 mm. of Hg. The sp. ht. of the metal was found to be 0.152. Calculate the equivalent and at. wt. of the element.
Eq. wt. = 20.15 ; *at. wt.* = 40.3.

13. The chloride of a metal contains 54.42% chlorine (at. wt. 35.5). The vapour density of the chloride is 8.16 (O = 1). Calculate the equivalent weight of the metal and the molecular formula of the chloride.
Madras Inter. ; *eq. wt.* 29.73 ; MCl_4.

14. In an experiment 2.470 gm. of copper oxide was obtained by oxidising 1.986 gm. of copper by nitric acid ; 0.335 gm. of copper was precipitated by 0.346

gm. of zinc from a solution of copper sulphate. Find the equivalent of copper and zinc.
Cu = 32.8 ; Zn = 33.88.

15. The equivalent weight of a volatile metal is 100.3. The specific heat of the metal is 0.033. 0.25 gm. of the metal occupies 79.5 c.c. at 500°C and 760 mm. Calculate the atomic weight of the metal and the molecular weight of its vapour.
At. wt. = 200.6 ; mol. wt. = 199.5.

16. A certain metal forms two oxides. When 0.5 g. of the first oxide was heated in hydrogen, 0.1687 g. of water was obtained, while 0.4 gm. of second oxide under similar conditions yielded 0.1000 g. water. Calculate the equivalent of the metal.
Gauhati 1952. 18.66 ; 28.

17. 363 c.c. of H_2 at 15°C and 756 mm. were liberated from dilute H_2SO_4 by 1 g. of zinc ; 0.973 g. of Cu was deposited by the action of a solution of copper sulphate on 1 gm. of zinc. Calculate the equivalent of zinc and copper.
Lond. Mat. Zn 32.44 ; Cu 31.56.

18. 1 g. of the chloride of a bivalent metal when treated with excess of silver nitrate, gave 0.965 g. of AgCl. Calculate atomic weight of metal, Ag = 107.9 and Cl = 35.5.
Punjab Inter. 1932 ; 226.2.

19. On heating in contact with tin, sulphuretted hydrogen (density 17) is converted into hydrogen without change of volume. Calculate the equivalent weight of sulphur.
Cal. 1945 ; 16.

20. State the relationship between the atomic weight, equivalent weight, and valency of the element. 0.1755 g. of a bivalent metal and 0.1316 g. of a trivalent metal when separately placed in dilute hydrochloric acid, yielded the same volume of hydrogen, viz., 190 c.c. at 27°C and 720 mm. pressure. Find the equivalent and atomic weights of the metals.
Calcutta '52.
Bivalent metal : eq. wt. 12 ; at. wt. 24 ; trivalent metal : eq. wt. 9 ; at. wt. 27.

IX

ELECTROLYSIS AND THE IONIC THEORY

Substances are grouped as conductor and non-conductor according as they conduct electric current or not. There are, again, two types of conductors :

(i) **Metallic conductors.**—Substances which conduct current without undergoing any permanent change are called *metallic conductors.* Electricity is carried by electrons in metallic conductors. All metals and a few substances which are not definitely metallic such as gas carbon and selenium, belong to this class.

Pure water is such a feeble electrolyte that it is often classed as a non-conductor. Mercury is a good conductor but not an electrolyte. Anhydrous hydrofluoric acid, alcohol, sugar solution, etc., are examples of a non-conductor.

(ii) **Electrolytes.**—Compounds which in *solution* or in the *fused state* conduct electric current and undergo simultaneous decomposition are called *electrolytes ;* electrolytes may be acids, bases and salts. Salts and alkalis which are bad conductors when solid, are excellent electrolytes when fused. Aqueous solutions of acids, bases and salts are also good electrolytes. Electricity is carried by ions in electrolytes.

Electrolysis.—When an electric current is passed into an aqueous solution of zinc chloride by dipping two platinum plates—one connected with the positive and the other to the negative pole of a battery—into the solution, decomposition occurs with the liberation of zinc and chlorine. The platinum plates leading the current in and out of the solution are called *electrodes*—the electrode connected to the positive pole of the battery is charged with positive electricity and is called the **anode,** and that connected with the negative pole of the battery is charged with negative electricity and is called the **cathode.**

The solution of the electrolyte zinc chloride undergoes reversible dissociation, yielding ions (electrically charged atoms or radicals) of opposite charges : $ZnCl_2 \leftrightharpoons Zn^{++} + 2Cl^-$.

The positively charged ions are called **cations** while the negatively charged ions are called **anions.** The cation, viz., the Zn^{++} ion, migrates to the cathode and gets discharged on its surface and becomes converted to a zinc atom. The anion, viz., Cl' ion moves to the anode and is discharged on its surface as an atom of chlorine—the atoms combine to form a molecule which is liberated as gas.

At cathode $Zn^{++} + 2e = Zn$;

At anode $Cl^- - e = Cl$; $Cl + Cl = Cl_2$.

where *e* represents a unit of negative charge, called an *electron.*

The electricity is, therefore, carried across from one electrode to the other by the ions, and hence the moving ions constitute the current in the electrolyte. Fused zinc chloride behaves similarly. *Such a process of conduction of an electric current by an electrolyte either fused or in solution, and the accompanying chemical decomposition* are called electrolysis.

Ions.—Ions are electrically charged atoms or radicals, (i.e., atoms or group of atoms which have gained or lost electrons, thus acquiring negative or positive charges, respectively) usually produced during the reversible dissociation of an electrolyte in its aqueous solution or in the fused state.

The electrolyte resolves into ions of opposite charges—the metals and hydrogen produce cations and the non-metals and acid radicals anions. The ions are the carriers of electric current in electrolysis. When an electric current is passed through an electrolyte the cations deposit at the cathode and are called *electro-positive groups* while the non-metals and acid radicals appear at the anode and are called *electro-negative groups.* Hence, *metals are electro-positive and non-metals electro-negative.*

$H_2SO_4 \leftrightharpoons 2H^+$ (cation) $+ SO_4^{--}$ (anion).

$NaCl \leftrightharpoons Na^+$ (cation) $+ Cl^-$ (anion).

$Ca(NO_3)_2 \leftrightharpoons Ca^{++}$ (cation) $+ 2NO_3^-$ (anion).

The hydroxyl ion OH^-, is an anion, and is discharged at the anode during electrolysis. $NaOH \leftrightharpoons Na^+ + OH^-$.

Theory of electrolytic dissociation.—To explain the phenomenon of electrolysis the Swedish chemist *Arrhenius* (1887) put forward the theory of electrolytic dissociation which states :

(i) The molecules of an electrolyte such as an acid, base or salt when dissolved in water, mostly split up or dissociate spontaneously into postively and negatively charged ions—the ions produced remaining in equilibrium with the undissociated molecules. This phenomenon is called **electrolytic dissociation,** and is *reversible* in character. Molecules of sodium chloride, sulphuric acid, copper sulphate, caustic soda, for example, dissociate in their aqueous solutions in the following way :

$NaCl \leftrightharpoons Na^+ + Cl^-$; $NaOH \leftrightharpoons Na^+ + OH^-$

$CuSO_4 \leftrightharpoons Cu^{++} + SO''_4$ $H_2SO_4 \leftrightharpoons 2H^+ + SO_4''$

Since the solution as a whole is uncharged, the sum of the charges on the cations must be equal to the sum of the charges on the anions.

(ii) The degree of ionisation, i.e., the extent to which an electrolyte dissociates into ions, largely depends on such factors as dilution, temperature, presence of other ions in solution, and above all, on the nature of the electrolyte and the ionising medium. Many acids, bases and salts such as hydrochloric acid, caustic soda and common salt, show a very high degree of ionisation even at ordinary dilution, and are called **strong electrolytes,** whereas substances like acetic acid and carbonic acid ionise to a very small extent only and are known as **weak electrolytes.** The electrolytic dissociation, also called **ionisation,** steadily increases with dilution up to an '*infinite dilution*', i.e., up to a very great *dilution*, when the electrolyte *completely* splits into ions. Ionisation is practically complete in a very dilute solution. Ionisation is helped by rise of temperature.

(iii) It is the ions which conduct current during electrolysis—the undissociated molecules taking no part in the conduction. In general the greater the dilution or higher the temperature, the greater is the degree of ionisation and hence also the higher is the conductivity of the solution. The cations and the anions migrate to the cathode and the anode respectively during electrolys is and are discharged there.

It is useful to remember that *hydrogen and the metals are deposited at the cathode, and the acid radicals are liberated at the anode.*

According to Arrhenius's theory any reaction between electrolytes in solution is a *reaction between ions*—it is really the ions that interact. When silver nitrate is added to sodium chloride solution, a white precipitate of silver chloride is formed, since the silver ion reacts with the chloride ion forming insoluble silver chloride :

$AgNO_3 \rightleftharpoons Ag^+ + NO_3'$; $NaCl \rightleftharpoons Na^+ + Cl^-$

$Ag^+ + Cl^- \rightleftharpoons AgCl$; $HCl \rightleftharpoons H^+ + Cl^-$

$AgNO_3$ is the reagent for chloride ion, Cl' and precipitates it as silver chloride from an aqueous solution of a chloride, *independent of its cation ;* thus solutions of HCl, KCl, $CaCl_2$ etc., all give a precipitate with silver nitrate. Potassium chlorate, $KClO_3$, on the other hand, though it contains chlorine, gives no precipitate with silver nitrate, since on ionisation it yields chlorate ion, ClO_3' and *no chloride ion.*

$$KClO_3 \rightleftharpoons K^+ + ClO_3^-$$

Silver nitrate is a reagent for chloride ion and not for chlorine merely. Similarly, barium chloride is the reagent for sulphate ion and gives a precipitate of barium sulphate with sulphuric acid or its salt in solution.

$$H_2SO_4 \rightleftharpoons 2H^+ + SO_4'' ; \qquad BaCl_2 \rightleftharpoons Ba^{++} + 2Cl^-$$
$$Ba^{++} + SO_4'' \rightleftharpoons BaSO_4$$

Illustrations of electrolysis.—(i) **Electrolysis of water.** Water is a *feeble* electrolyte, and only slightly dissociates into H^+ and OH^- ions : $H_2O \leftrightharpoons H^+ + OH^-$. Its conductivity is increased by adding dilute sulphuric acid which dissociates greatly yielding H^+ and SO_4'' ions :

$$H_2SO_4 \leftrightharpoons 2H^+ + SO_4''.$$

During electrolysis using platinum electrodes the hydrion, H^+ is discharged at the cathode as an atom of hydrogen—the atoms form molecules which are evolved as gas : of the hydroxyl, OH', and the sulphate, SO_4'', ions, the hydroxyl ions, OH^-, are prefrentially discharged at the anode—the OH radicals then react with one another forming water and evolving oxygen.

At cathode $H^+ + e = H$; $H + H = H_2$

At anode $OH^- - e = OH$; $4OH = 2H_2O + O_2$

Same consideration applies to the electrolysis of dilute sulphuric acid.

(ii) **Electrolysis of sodium chloride.**—The aqueous solution of sodium chloride dissociates, yielding Na^+ and Cl' ions, and water furnishes H^+ and OH^- ions :

$$NaCl \leftrightharpoons Na^+ + Cl' ; \quad H_2O \leftrightharpoons H^+ + OH^-$$

During electrolysis with *graphite electrode* H^+ ions, *and not the* Na^+ *ions*, are preferentially dicharged at the cathode, and the hydrogen is liberated as a gas. The chloride ions are discharged at the anode—the chlorine evolves as a gas at the anode.

At cathode $H^+ + e = H$; $H + H = H_2$

At anode $Cl^- - e = Cl$; $Cl + Cl = Cl_2$

The solution after electrolysis, therefore, contains Na^+ and OH' ions, i.e., caustic soda, $NaOH \leftrightharpoons Na^+ + OH^-$

During electrolysis with *mercury cathode*, as in Castner-Kellner cell, the Na^+ ions, *and not the* H^+ *ions*, are preferentially discharged at the cathode—the liberated sodium dissolves in the mercury and forms an amalgam. The amalgam is then decomposed by water, giving caustic soda and hydrogen.

The chloride ions Cl^- are discharged, as usual, at the graphite anode, and the chlorine is liberated as a gas.

(iii) **Electrolysis of copper sulphate.**—Copper sulphate yields on icnisation, Cu^{++} and SO_4'' ions ; watr yields H^+ and OH^- ions. Hence the solution contains these four ions.

$$CuSO_4 \leftrightharpoons Cu^{++} + SO_4'' : H_2O \leftrightharpoons H^+ + OH'.$$

During electrolysis *at copper electrodes* copper ions are discharged at the cathode and liberated as a deposit of metallic copper, while at the anode copper atoms pass into solution as cupric ions Cu^{++}, —sulphate ions are not discharged since the negative charges are removed more easily from a copper atom than from a sulphate ion SO_4''.

At cathode $Cu^{++}+2e = Cu$; At anode $Cu-2e = Cu^{++}$
Hence, during electrolysis of copper sulphate, copper dissolves at the anode and deposits at the cathode.

During electrolysis *at platinum anodes,* cupric ions are discharged as usual at the cathode, while OH^- ions, *and not the* SO_4'' *ions,* are preferetially discharged at the anode—the OH groups then react to form water and oxygen which evolves as a gas.

During electrolysis the Cu^{++} ions and the OH^- ions are discharged, and consequently the solution contains the H^+ and SO_4'' ions, i.e., sulphuric acid after electrolysis.

(iv) **Electrolysis of caustic soda.**—The aqueous solution of caustic soda contains, H^+, OH^- and Na^+ ions ;

$$H_2O \leftrightharpoons H^+ + OH' \text{ ; } NaOH \leftrightharpoons Na^+ + OH'.$$

On electrolysis OH' ions are discharged at the anode—OH radicals react evolving oxygen, while the H^+ ions (and *not* Na^+ ions) are preferentially discharged at the cathode. Hence the electrolysis of caustic soda solution evolves hydrogen and oxygen only.

Ampere and Coulomb.—The practical unit of current, called the **ampere,** defined as the current which, flowing uniformly for 1 second, deposits 0.001118 gram of silver from a solution of silver nitrate. The unit quantity of electricity, called the **coulomb,** is the quantity of electricity passing when 1 ampere flows for 1 second. If q coulombs of electricity pass when c amperes flow for t seconds, then

$$q = c \times t$$

$$\text{Coulomb} = \text{ampere} \times \text{second}$$

Faraday's laws of electrolysis.—As a result of his investigations on electrolysis Michael Faraday in the year 1832 enunciated two laws indicating the relation between the quantity of electricity passing through an electrolyte and the amount of any substance liberated at the electrode.

First law.—*The weight of an ion deposited or formed at an electrode is directly proportional to the quantity of electricity passing through an electrolyte, i.e.,* $w \propto q$,

where w = weight in gram of the ion liberated by q coulombs of electricity when a uniform current of c amperes flow for t seconds.

$$\therefore \quad q = c \times t \text{ ; but } w \propto q \text{ ; } \quad \therefore \quad w \propto c \times t \text{ ; or } w = z \times c \times t,$$

when z is a constant and is called the *electrochemical equivalent.*

For the passage of same (q) quantity of electricity the weights (w_1 and w_2) of 2 ions deposited are proportional to their electro-chemical equivalents (z_1 and z_2).

$$w_1 = z_1 q \text{ and } w_2 = z_2 q \text{ ; } \quad \therefore \quad w_1/w_2 = z_1/z_2$$

Electrochemical equivalent.—When $c = 1$ ampere and $t = 1$ second, z becomes equal to w gms. Hence *the electro-chemical equivalent (E. C. E.) of an element is its weight in grams which is liberated by the passage of one coulomb of electricity through the electrolyte,* i.e., by a uniform current strength of one ampere flowing for one second. Thus 1 coulomb of electricity deposits from a solution of silver nitrate 0.001118 gram of silver, which is, therefore, the E.C.E. of silver.

The E. C. E. of hydrogen = 0.0000104.
The E. C. E. of silver = 0.001118 gm.

Second law.—*The weights of different ions deposited or formed at the electrodes, when the same quantity of electricity passes through different electrolytes are proportional to their chemical equivalents.*

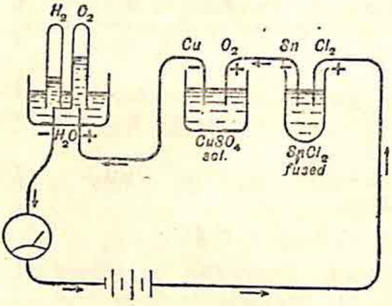

Fig. 34.

Three electrolytic cells—the first one containing acidulated water, the second a solution of copper sulphate, the third fused stannous chloride—are connected in series so that the same current passes through all of them. After electrolysis for some time, the volumes of hydrogen and oxygen liberated from the acidulated water, and the weights of copper and tin deposited from the copper sulphate solution and the fused stannous chloride respectively, are determined (fig. 34).

It is found that when 1.008 gm. of hydrogen is evolved, the weights of oxygen, copper and tin liberated are 8,31.78 and 59.3 gms. respectively—8,31.78 and 59.3 being the chemical equivalents of oxygen, copper and tin respectively. Hence the verification of the second law.

Let w_1 and w_2 be the weights of two elements (of equivalent weights E_1 and E_2 respectively) deposited by the same quantity (q coulombs) of electricity. Then

$$w_1/w_2 = E_1/E_2$$

But according to the first law ($w=zq$), for the passage of the same (q coulombs) quantity of electricity the weights of ions liberated are proportional to their electrochemical equivalents, i.e.,

$$w_1/w_2 = z_1/z_2 \; ; \quad \therefore \quad z_1/z_2 = E_1/E_2$$

When one of the substances liberated is hydrogen for which $E = 1.008$, and $z = 0.0000104$, the relation becomes :

$$z/0.0000104 = E/1.008$$

$$\therefore \quad z = E \times 0.0000104/1.008$$

or electrochemical equivalent = *chemical equivalent* × 0.0000104 nearly.

Combination of Faraday's laws.—Since $w \propto ct$ (*first law*) and *also* $w \propto E$ (*second*), the combination of the two laws of electrolysis leads to the relation :

$$w \propto ct\,E. \quad \text{or} \quad w = ct\,E/F,$$

where $1/F$ is the proportionality constant.

Taking the quantity of electricity ct equal to F, w becomes equal to E., i.e., the weight of a substance deposited or dissolved is equal to the equivalent weight. Therefore, *F, called the* **faraday,** *is the quantity of electricity required to deposit or dissolve* 1 *gram equivalent of a substance in electrolysis.*

1 coulomb of electricity deposits 1 electro-chemical equivalent, i.e., 0.00118 gram. of silver in electrolysis. Therfore, the quantity of electricity required to deposit 1 gram equivalent, i.e., 107.88 grams of silver, and hence 1 gram equivalent of any substance, is

$107.88 \div 0.001118 = 96494$ coulombs, which is usually rounded off to 96500, i.e., $F = 96500$ coulombs.

96500 *coulombs*, i.e., 1 *faraday of electricity*, therefore, *deposits or forms* 1 *gram equivalent of an ion in electrolysis.*

$$\therefore \quad w = \frac{ctE}{96500}$$

Determination of equivalent weight.—The equivalent weights of elements may be determined electro-chemically in two ways from the relation :

$$\text{(i) } z = E \times 0.0000104/1.008 \; ; \quad \text{(ii) } w_1/w_2 = E_1/E_2.$$

The equivalent weight of copper.—(i) The equivalent weight of copper may be determined by finding its electro-chemical equivalent in the following way.

The two copper electrodes of a copper voltameter which is a glass vessel containing a solution of copper sulphate which has been acidified with dilute sulphuric acid, are connected to the two terminals of a battery through an adjustable resistance and ammeter. The cathode which is a pure copper plate, is carefully cleaned, dried and weighed before the experiment, and then placed into the copper sulphate solution. A definite amount of current which is read from the ammeter, is sent through the copper sulphate solution for a given period of time.

After electrolysis, the cathode with a deposit of copper on it, is taken out, washed with distilled water, dried and weighed again——the difference in weight gives the weight of copper deposited. Suppose :

the copper deposited	...	... w grams.
the current passed	...	... c amperes.
the time	...	... t seconds.

$\therefore$ $w = zct$ or $z = w/ct$; where z = electro-chemical equivalent of copper.

Knowing z of Cu from $z = w/ct$, the E of Cu is determined from the relation : z of Cu = E of Cu $\times 0.0000104/1.008$.

(ii) Two electrolytic cells, one containing copper sulphate solution and the other silver nitrate solution, are connected in series through an adjustable resistance and an ammeter. The same amount of electricity is sent through the two cells for a given time. The weights of copper and silver deposited on the respective cathodes are determined after electrolysis. Then by the second law of electrolysis :

$$\frac{\text{weight of Cu deposited}}{\text{weight of Ag deposited}} = \frac{\text{chemical equivalent of Cu}}{\text{chemical equivalent of Ag}}$$

Taking the chemical equivalent of silver to be 107.88, that of copper may be found out.

Dissociation.—There are many substances the molecules of which split up on heating into simpler molecules or atoms which, however, recombine on cooling—the phenomenon is called *dissociation*, or what is called *thermal dissociation*. The process of dissociation is *reversible* in character—the products of dissociation remain in equilibrium with the undissociated molecules.

Thus when ammonium chloride is heated, a fraction of its molecules dissociates into ammonia and hydrochloric acid which remain in equilibrium with the undissociated molecules of the ammonium chloride. $NH_4Cl \leftrightharpoons NH_3+HCl$.

Calcium carbonate dissociates on heating into calcium oxide and carbon dioxide ; phosphorus pentachloride dissociates by heat into phosphorus trichloride and chlorine.

$$PCl_5 \leftrightharpoons PCl_3+Cl_2 \qquad CaCO_3 \leftrightharpoons CaO+CO_2$$

Iodine dissociates into atoms of iodine on heating :

$$I_2 \leftrightharpoons I+I.$$

The thermal dissociation *differs* from ionisation in the following respects :

(i) Products of thermal dissociation are neutral atoms or molecules, while those of ionisation are electrically charged atoms or radicals, called ions.

(ii) Products of thermal dissociation are separable by physical means, such as solution, diffusion, etc., thus, the products of dissociation of ammonium chloride, ammonia and hydrochloric acid may be separated, partially though, by the process of diffusion, while the products of ionisation cannot be separated by such physical processes because of the existence of strong electrostatic attraction between the oppositely charged ions.

(iii) Thermal dissociation requires no medium, while in ionisation the electrolyte is dissolved in an ionising solvent or is fused.

Both the processes are, however, *reversible* in character.

Decomposition.—The process ordinarily sginifies the breaking up of a substance by heat into simpler substances which do not recombine on cooling and hence the process is *irreversible*.

Thus, ammonium nitrate decomposes by heat irreversibly into water and nitrous oxide ; potassium chlorate breaks up on heating into potassium chloride and oxygen.

$$NH_4NO_3 = N_2O+2H_2O \text{ ; } 2KClO_3 = 2KCl+3O_2.$$

Acids, bases and salts.—Certain properties of acids and bases have already been mentioned (p. 28).

Acids are generally soluble in water—the solution has a sour taste, turns blue litmus red, and conducts electric current, since it dissociates into ions e.g.,

$$HCl \leftrightharpoons H^+ + Cl^- \text{ ; } H_2SO_4 \leftrightharpoons 2H^+ + SO_4''$$

Acids yield H^+ ions (also called, *protons*) on ionisation in aqueous solution ; hence *an acid may be defined as a hydrogen-containing compound which dissociates in aqueous solution with the formation of hydrogen ions as the only positive ion. An acid*, therefore, *may be defined as a proton donor.*

An alkali ionises in aqueous solution yielding the hydroxyl (OH') ions and no other negative ion, and conducts electric current.

$$NaOH \leftrightharpoons Na^+ + OH' \text{ ; } \quad Ca(OH)_2 \leftrightharpoons Ca^{++}+2OH^-$$

A base may, therefore, be defined as a compound which, when dissolved in water undergoes dissociation with the formation of hydroxyl ions OH^- as the only negative ion.

Since the OH′ ion of a base always reacts with H^+ ion of an acid producing water, *a base may be defined as a proton acceptor.*

Strength of acids and bases.—An acid in solution owes its acidic properties to the hydrogen ions it yields. Therefore the amount of H^+ ions formed by the ionisation (electrolytic dissociation) of an acid in aqueous solution may be taken as a measure of its strength—the greater the quantity of H^+ ions in the solution the stronger the acid. Hence acids which are highly dissociated in solution yielding large amount of H^+ ions are termed **strong acids,** while those which are but slightly dissociated are known as **weak acids.** The degree of dissociation is, therefore, a measure of the strength of an acid. The mineral acids HCl, HNO_3 and H_2SO_4 are strong acids, while the organic acids, oxalic acid and acetic acid are weak acids. Carbonic acid is a weak acid ; hydrocyanic acid, HCN, is weaker still.

The concentration of OH′ ions in solution is a measure of the strength of an alkali ; NaOH and KOH are strong alkalis since they are largely ionised even in moderate dilution, while NH_4OH is a weak alkali.

Neutralisation.—When solutions of an acid and an alkali are mixed together in equvialent proportions the resulting solution has neither acid nor alkaline character—this reaction is called *neutralisation* which involves the formation of salt and water by interaction between the acid and the alkali :

$$NaOH + HCl = NaCl + H_2O$$

The acidic property of a solution is due to the presence of H^+ ions while the alkalinity is due to OH^- ions in a solution. Water is neutral since it contains H^+ and OH^- ions in equal amounts :

$$H_2O \leftrightharpoons H^+ + OH^-$$

When equivalent amounts of acids and alkalis are mixed together in aqueous solution, the H^+ ions of the acid react with the OH^- ions of the alkali forming water—the process is called neutralisation and the solution is neutral, since it does neither contain H^+ nor OH^- ions in excess. Hence neutralisation is defined as a process which involves the formation of practically undissociated molecules of water from H^+ and OH^- ions of equivalent amounts of acids and alkalis respectively.

$$H^+ + Cl^- + Na^+ + OH^- \leftrightharpoons Na^+ + Cl^- + H_2O$$
$$\textit{i.e.,}\ H^+ + OH^- \leftrightharpoons H_2O$$

Basicity of acids and acidity of bases.—Basicity of an acid is its power of neutralising a base and is measured by the number of replaceable hydrogen atoms in the molecule of an acid, i.e., by the number of hydrogen ions that one molecule of an acid can *give to a base* ; e.g., sulphuric acid H_2SO_4 is *dibasic,* since it can yield two H^+ ions in solution ; phosphoric acid H_3PO_4, is *tribasic ;* hydrochloric HCl and nitric acids HNO_3 are *monobasic.* Acids with one, two, and three replaceable hydrogen atoms are known as *monobasic, dibasic, and tribasic* acids respectively.

An acid is said to be **polybasic** when a molecule of it yields more than one H^+ ion on ionisation ; a polybasic acid may ionise in stages :

$$H_2SO_4 \leftrightharpoons H^+ + HSO_4^-. \qquad HSO'_4 \leftrightharpoons H^+ + SO_4''$$

Acidity of a base is its power of neutralising an acid and is measured by the number of replaceable hydrogen atoms of an acid with which a molecule of a base can react, i.e., by the number of hydrogen ions which one molecule of a base can accept from an acid. By this definition, caustic soda, NaOH, caustic potash, KOH and ammonia are *monoacidic ;* sodium carbonate, Na_2CO_3 and calcium hydroxide, $Ca(OH)_2$ are *diacidic*, freric hydroxide, $Fe(OH)_3$ *triacidic*. In the case of hydroxides the number of OH groups in a molecule represent its acidity.

Salt.—*A salt is a compound produced from an acid by the replacement of a part or whole of its replaceable hydrogen atoms by a metal or a basic radical.* A salt, therefore, consists of a metallic (or basic radical) linked to a non-metallic (or an acidic) radical. In zinc sulphate, for example, Zn is the basic radical and SO_4 the acidic radical ; in sodium nitrate Na is the basic radical and NO_3 the acidic radical. Salts dissociate into ions in solution :

$ZnSO_4 \leftrightharpoons Zn^{++}$ (basic radical) $+SO_4''$ (acidic radical).

$NaNO_3 \leftrightharpoons Na^+$ (basic radical) $+NO'_3$ (acidic radical).

Types of salts.—Three types of salts are distinguished.— (i) **Acid salts.**—Acid salts are formed by the partial replacement of the replaceable hydrogen atoms of a polybasic acid by a metal or ammonium and as such they contain some replaceable hydrogen atoms : hence an acid salt has the properties of salts in addition to those of acids. They are also known as **bisalts.** Examples are : sodium bicarbonate, $NaHCO_3$; sodium bisulphate (sodium hydrogen sulphate), $NaHSO_4$; disodium hydrogen phosphate, Na_2HPO_4. An acid salt is produced when a polybasic acid reacts with a quantity of a base insufficient to replace the whole of replaceable hydrogen atoms.

$$NaOH + H_2SO_4 = NaHSO_4 + H_2O.$$
$$NaOH + H_2CO_3 = NaHCO_3 + H_2O.$$

(ii) **Normal Salts.**—Normal salts are formed by the replacement of all the replaceable hydrogen atoms of an acid by a metal or ammonium. It thus contains neither the replaceable hydrogen atoms of an acid nor the oxygen or hydroxyl of a base. A normal salt is produced when equivalent amounts of acids and bases react :

$$2NaOH + H_2SO_4 = Na_2SO_4 + 2H_2O$$
$$2NaOH+H_2CO_3 = Na_2CO_3+2H_2O \ ; \ NaOH+HCl = NaCl+H_2O.$$

Na_2SO_4, Na_2CO_3, NaCl—all are normal salts.

(iii) **Basic salts.**—Basic salts contain an excess of a base, i.e., oxygen or hydroxyl radical which may be replaced by acidic radicals forming normal salts. A basic salt is produced when a polyacid base is only partially neutralised by an acid.

$$Pb(OH)_2 + HCl = Pb(OH)Cl \text{ (basic lead chloride) } + H_2O.$$

White lead, $2PbCO_3$, $Pb(OH)_2$ and bismuth oxychloride, $BiOCl$, are basic salts. They are generally insoluble in water but dissolve in acids.

Bismuth oxychloride is produced as a white turbidity on diluting a solution of bismuth chloride with water—the turbidity, however, dissolves in the acid. $BiCl_3 + H_2O \leftrightharpoons BiOCl + 2HCl$.

Hydrolysis of salts.—It might be expected that solutions of *normal salts* should be neutral in reaction, since they contain no replaceable hydrogen atoms nor any OH of a base. But this is true only in the case of *salts of strong acids and strong bases only ;* such salts simply ionise in solution :

$$NaCl \rightleftharpoons Na^+ + Cl^- ; \qquad Na_2SO_4 \rightleftharpoons 2Na^+ + SO_4''$$

Salts of weak acids or weak bases or both are *reversibly* split up by water with the formation of free acid and free base :

$$NaCN+HOH \rightleftharpoons NaOH+HCN$$

$$FeCl_3+3HOH \rightleftharpoons Fe(OH)_3+3HCl$$

and the process is called **hydrolysis**—the solution reacts *acidic* or *alkaline* according as the acid or base is relatively strong. Three cases of salt hydrolysis occur :

(i) **Salt of a weak acid and a strong base.**—Salts of weak acids (oxalic, acetic, carbonic, hydrocyanic, etc.) and strong bases (NaOH and KOH, etc.) are *alkaline* in reaction in their aqueous solution, since they are partially hydrolysed by water producing a *strong base* and a weak acid, e.g.

$$NaCN+HOH \rightleftharpoons NaOH+HCN \text{ (weak acid)}$$

$$Na_2CO_3+2HOH \rightleftharpoons 2NaOH+H_2CO_3 \text{ (weak acid).}$$

Solutions of sodium cyanide, NaCN, and sodium carbonate, therefore, react alkaline to litmus.

Owing to hydrolysis sodium carbonate behaves like a weak alkali in solution.

(ii) **Salt of a strong acid and a weak base.**—Salts of strong acids (HCl, HNO_3, H_2SO_4, etc.) and weak bases (metals like iron, aluminium, copper, etc., i.e., metals other than alkali metals, Na, K, etc. and the alkaline earth metals, Ba, Sr, Ca, etc., make weak bases) are all *acidic* in reaction in their solution, since they are partially split up by water producing a *strong* acid and a weak base, e.g.,

$$FeCl_3+3HOH \rightleftharpoons Fe(OH)_3 \text{ (weak base)}+3HCl.$$

$$CuSO_4+2HOH \rightleftharpoons Cu(OH)_2 \text{ (weak base)}+H_2SO_4.$$

Aqueous solution of ferric chloride and copper sulphate are, therefore, acidic to litmus.

(iii) **Salts of a weak acid and a weak base** is split by water into acid and base which are both weak—the solution may, therefore, be *neutral* when both are equally weak. Ammonium acetate solution is approximately neutral :

$$CH_3COONH_4 + HOH \rightleftharpoons CH_3COOH + NH_4OH$$

Ammonium formate solution reacts slightly acid, since ammonium hydroxide is weaker than formic acid.

$$HCOONH_4 + HOH \rightleftharpoons HCOOH + NH_4OH$$

Acid salts possess the properties of salts in addition to those of acids but are not necessarily acidic in reaction. $NaHSO_4$, for example, is acidic to litmus, since it ionises yielding H^+ ions :

$$NaHSO_4 \rightleftharpoons Na^+ + HSO_4^- ; \quad HSO_4^- \rightleftharpoons H^+ + SO''_4$$

Sodium bicarbonate, though an acid salt, reacts feebly alkaline to litmus in solution, owing to hydrolysis :

$$NaHCO_3 + HOH \rightleftharpoons H_2CO_3 + NaOH.$$

Exercises

(1) The same amount of electricity which liberated 100 c.c. of oxygen collected over water at 15°C and 750 mm of mercury, deposited 1.772 gm. of silver. Calculate the equivalent of silver. 1 c.c. of oxygen at N.T.P. weighs 0.001429 gm. Tension of aqueous vapour at 15°C = 13 mm.

$$\text{Volume at N.T.P. of oxygen liberated} = \frac{100 \times 273(750-13)}{288 \times 760} = 91.94 \text{ c.c.}$$

Weight of oxygen = $91.94 \times 0.001429 = 0.1314$ gm.

$$\frac{\text{Equivalent of Ag}}{8} = \frac{1.772}{0.1314}\text{; Equivalent of Ag} = 107.9$$

(2) Two cells, one containing copper sulphate and the other silver nitrate, were placed in the same circuit. It was found that 0.106 g. of Cu was deposited in the same time as 0.3597 g. of Ag. Calculate equivalent of silver and also find out the amount of silver which will be deposited when a current of 1.05 amperes is passed through the solution of silver nitrate for 20 minutes. Equivalent weight of copper = 31.8. *Calcutta* 1953.

$$\frac{\text{Equivalent of Ag}}{\text{Equivalent of Cu}} = \frac{\text{wt. of Ag deposited}}{\text{wt. of Cu deposited}}$$

$$\therefore \quad \frac{\text{Equivalent of Ag}}{31.8} = \frac{0.3597}{0.106} \qquad \therefore \quad \text{Equivalent of Ag} = 107.9.$$

$$\frac{\text{E.C.E. of Ag}}{\text{E.C.E. of } H_2} = \frac{\text{Eq. wt. of Ag}}{\text{Eq. wt. of } H_2}\text{ i.e., } \frac{\text{E.C.E. of Ag}}{0.0000104} = \frac{107.9}{1.008}$$

$\therefore$ E.C.E. of Ag = 0.001114,

and wt. of Ag = $0.001114 \times 1.05 \times 20 \times 60 = 1.404$ gm.

Alternatively, from the relation w = Ect/96500,

$$w = 107.9 \times 1.05 \times 20 \times 60/965000 = 1.409 \text{ gm.}$$

(3) A current of 0.5 ampere is sent through a solution of copper sulphate for 20 minutes using platinum electrodes.

(i) Calculate weight of copper deposited at the cathode.
From the relation w = ct E/96500

$$\text{Weight of Cu} = \frac{0.5 \times 20 \times 60}{96500} \times \frac{63.57}{2} = 0.1977 \text{ g.}$$

(ii) Calculate number of copper atoms deposited.

1 gram atom, i.e., 63.57 gm. of Cu contain 6.023×10^{23} atoms.

$\therefore$ 0.1977 g. of Cu contain $0.1977 \times 6.023 \times 10^{23} 63{\cdot}57 = 0.1873 \times 10^{22}$ atoms.

(iii) Calculate volume of oxygen liberated at the anode at 27°C and 756 mm.

$$\frac{\text{Wt. of } O_2 \text{ liberated}}{\text{Wt. of Cu deposited}} = \frac{\text{Eq. wt. of } O_2}{\text{Eq. wt. of Cu}}$$

$\therefore$ wt. of O_2 liberated = $8 \times 0.1977/31.78 = 0.0497$ g.

Volume of O_2 at N.T.P. = $0.0497 \times 22400/32 = 34.79$ c.c.

$$\therefore \quad \text{Volume at 27°C and 756 mm} = \frac{34.79 \times 760 \times 300}{756 \times 273} = 37.55 \text{ c.c.}$$

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4. Explain and illustrate what you understand by electrolysis. State Faraday's laws of electrolysis. How would you determine the chemical equivalent of copper electro-chemically ? *Calcutta* '43 ;

5. Write short notes on (i) dissociation and decomposition; (ii) electrochemical equivalent. Deduce a relation between electro-chemical equivalent of an element and its chemical equivalent. *Calcutta* '37

6. Give a short account of the ionic theory. Discuss in terms of the theory (a) strengths of acids and bases, (b) neutralisation, (c) hydrolysis.

7. A current of electricity deposits 0.2 gm. of copper (eq. wt. 31.8) from copper sulphate solution in half an hour. What volume of oxygen could be obtained using acidulated water and a current twice as strong as in the former case for 2 hours? If the gas were measured at 15°C and 765 mm. pressure how would the result be altered? 1 litre of oxygen at N.T.P. weighs 1.44 gm. *Ans.* 279.6 c.c. ; 292.9 c.c.

8. An electric current is passed simultaneously through the following solutions ; hydrochloric acid, ferrous sulphate, ferric sulphate, and silver potassium cyanide. If 5.2 litres of hydrogen at N.T.P. were evolved from the hydrochloric acid solution, how much metal would be deposited in the case of the iron and silver salts? Fe=56, Ag=108. *Ans.* Iron 13.0, 8.7 gms. ; silver 50.1 gm.

9. Explain what is meant by electrolysis. Show how electrolysis may be used to find the equivalent of a metal. What meaning does the statement : *the E.C.E. silver* is 0.001118 convey? Explain with illustrations the connection between valency and the charge of an ion.

10. Explain what you understand by the terms acid, base and salt. What are their characteristic properties? How are the salts classified? Classify the following salts—sodium bicarbonate, copper chloride, sodium nitrate.

11. An electric current is passed between platinum plates through solutions of copper sulphate, silver nitrate and dilute sulphuric acid, the solutions being placed in series. If 0.105 gm. of copper is deposited in the first cell, calculate : (a) the weight of silver separated from the second solution ; (b) the volume of hydrogen measured at 15°C and 740 mm. which is liberated from the third solution. Eq. wt. of Cu 31.8, and that of Ag 108. *Ans.* (a) 0.3567 gm. ; (b) 40 c.c.

12. A solution of a salt of a metal of atomic weight 112 was electrolysed for 150 minutes with a current of 0.15 ampere. The weight of metal deposited was 0.783 gm. Find the valence of the metal in the salt. *Ans.* 2

13. The same current is passed through acidulated water and through a solution of the chloride of metal X. The volume of hydrogen liberated at N.T.P. was 14.8 litres and the weight of metal deposited 42 gm. The specific heat of the metal is 0.094. Find the formula of the chloride. *Ans.* XCl_2.

14. What is the relation between : (a) electro-chemical equivalent and chemical equivalent of an element, (b) atomic weight and chemical equivalent of an element. Calculate electro-chemical equivalent of silver and oxygen, given E.C.E. of H = 0.0000104, and Ag = 108, O = 16.
Ans. E.C.E. of Ag = 0.00114 ; E.C.E. of O = 0.00008254. *Bombay* '31

15. An electric current is passed through solution of copper sulphate and cyanide of silver connected in series. If in a given time 0.35 g. of copper is deposited, what will be the weight of silver deposited in the same time? Cu = 63.57, Ag = 107.8. *Punjab* 1945. *Ans.* 1.187 gm.

16. What is meant by salt hydrolysis? Explain why an aqueous solution of sodium chloride is neutral towards litmus, a solution of sodium acetate is alkaline and a solution of ferric chloride is acidic.

17. State Faraday's laws of electrolysis and express them in the form of an equation. A current of 5 amperes is passed through a copper voltameter and a silver voltameter connected in series for 32 minutes and 10 seconds. Calculate the amount of Cu and Ag deposited. Given E.C.E. of Cu = 0.000325 g. and of Ag = 0.001118 g. *Calcutta* 1952, 1959. *Ans.* Cu 3.137 gm. ; Ag 10.79 gm.

18. A current of 2 amperes was passed through a solution of copper sulphate for 16 minutes and 5 secs. Calculate the amount of copper deposited on cathode. Given 96500 coulombs can deposit 63.6/2 gms. of copper. *Cal.* 1959. 0.636 gm.

X

ATOMIC STRUCTURE

In the nineteenth century the atom was regarded as a small indivisible particle—the unit of matter in all chemical changes. But convincing researches in physics of the celebrated scientists, Sir J. J. Thomson, Lord Rutherford and others equally famous in the beginning of the 20th century have shown that an atom is a complex structure.

Cathode rays : The electron.—When an electric discharge is sent through a rarefied gas (at low pressure of 0.1 mm. of Hg or less) in a vacuum tube, a stream of rays, called *cathode rays*, is emitted from the surface of the cathode and move in straight lines towards the anode. By studying the deflection in electric and magnetic fields Sir J. J. Thomson (1897) showed that the cathode rays consist of negatively charged particles. Each particle carries a negative charge of electricity of magnitude 1.6×10^{-19} coulombs which is equal but opposite to that of a hydrogen ion. These negatively charged particles are called *electrons*. The ratio of the charge e to the mass m of the electron, e/m, is 1.758×10^8 coulombs per gram. The ratio e/m for the electron is always the same, no matter what is the residual gas in a vacuum tube and the material of the cathode. The ratio e/m is 1836 times greater than the ratio of charge to mass, e′/m′, for the hydrogen ion, which is $96{,}494/1.008 = 9.574 \times 10^4$ coulombs. Since the charge of an electron is *equal* but opposite to that of the hydrogen ion, i.e., $e = e'$, its mass is 1836 times smaller.

$$\frac{e/m}{e'/m'} = \frac{1.758 \times 10^8}{9.574 \times 10^4} = 1836, \quad \therefore \quad m' = 1836\ m.$$

i.e., the hydrogen ion is 1836 times heavier than an electron.

Electrons can be had from all kinds of substances. *An electron is, therefore, a common constituent of all kinds of matter.* Hence *an electron is a constituent of all atoms.*

The positive rays : The Proton.—The discovery of the electron suggests that an atom contains positive electricity in some form since the atom as a whole is electrically neutral. Besides negatively charged cathode rays, the operation of a discharge tube always produces a stream of rays travelling in a direction opposite to the cathode rays, called *positive rays*. The *positive* rays consist of positively charged particles of atomic mass formed from atoms by the removal of electrons—the ratio of the charge to the mass of these particles is no longer constant as for the electron but depends on the nature of the residual gas in the tube. This ratio shows that these particles are much heavier than the electrons. The lightest positively charged particle has been detected in the hydrogen discharge tube—its mass it about the same as that of the hydrogen atom and it has a unit positive charge, i.e., *it is a hydrogen atom that has lost the electron. This particle of unit mass and unit positive charge* is known as a *proton.* No positively, charged ion has been found which has a mass less than that of a proton—the masses of different ions are integral multiples of that of proton. Hence, *protons like the electrons, enter into the structure of all kinds of atoms. A proton is a fundamental particle like an electron.* A proton with one electron forms a hydrogen atom and hence :

$$\text{mass of a H-atom} = \text{mass of a proton} + \text{mass of an electron}$$
$$= 1836\ \text{m} + \text{m} = 1837\ \text{m},$$

i.e., *the hydrogen atom is* 1837 *times heavier than the* electron.

The Neutron.—*Neutron* is another fundamental particle of matter, discovered by Chadwick in 1932 by bombarding beryllium with alpha particle (i.e., a particle of mass equal to 4 times that of a hydrogen atom and carrying 2 unit positive charges). The neutron has about the same mass as that of the proton, but no electric charge, i.e., it is a neutral particle of unit mass.

The structure of the atom.—The fundamental particles, electron, proton and neutron, enter into the structure of matter. The present conception about the structure of atom is mainly due to E. Rutherford (1911) and is based on his experiment on the *scattering of α-particles* by thin metal foils. When a thin gold foil, 0.0004 mm. in thickness, for example, is placed in the path of α-particles in a vacuum tube, most of the particles pass out practically without any deflection—a small proportion, however, are scattered through a large angle ; one α-particle in 20,000 was turned through 90° or more. This sudden and very large deflection suggests that the mass of the atom is located on a very minute nucleus, carrying the whole of the positive charge (fig. 35).

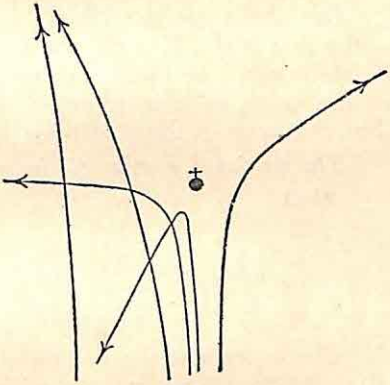


Fig. 35

The size of the nucleus must be very small indeed in comparsion with the atom, since the α-particles pass through several atoms without deflection—the diameter of the atom is of the order 10^{-8} cm. and that of the atomic nucleus is of the order of 10^{-12} cm. and hence the greater part of the atom is empty space. The atom is pictured as a system in which a tiny positively charged nucleus is surrounded by *planetary electrons*—an atom is, therefore, very much like a model of the solar system. Since an atom as a whole is electrically neutral, it must contain equal number of protons and planetary electrons. The planetary electrons revolve round the positively charged nucleus in a series of orbits in which they are held, not by gravity as in a solar system, but by electrostatic forces between the positive and negative charges.

Nucleus ←———————— Electron ————————→
+ Electrostatic attraction — Centrifugal force

The nucleus of an atom is built up of protons and neutrons—the mass of an atom being concentrated entirely in the nucleus. Since the neutrons, like protons, have unit mass but carry no electric charge, the *atomic mass* of an element is equal to the total number of protons and neutrons (the mass of electrons being negligibly small), while the number of protons is equal to the nuclear positive charge.

The proportion of protons and neutrons, however, can vary only within narrow limits, beyond which the nuclei are no longer stable, as in the case of heavy radioactive elements such as radium and uranium.

The atomic number *of an element is equal to the number of positive charges on the nucleus of an atom*, which is equal to the number of protons in the nucleus (also equal to the number of planetary electrons). Moseley showed that the atomic number is a more fundamental property of an element than its atomic weight.

The planetary electrons revolve in a set of concentric elliptical shells or orbits having the positive nucleus at one of the foci. There are seven such shells, each shell being able to contain a certain maximum number of electrons—the first shell which is the nearest orbit to the nucleus can contain only up to 2, the second up to 8, and so on.

The shells are described by the letters K, L, M, N, O, P, etc., —the first is the K shell, the second L, and so on ; *each shell represents a definite energy level*—the energy is the least when n = 1 and increases as the value of n increases, n being the serial number of the shell. The electrons in the K orbit are, therefore, at the lowest energy level.

The maximum number of electrons in a shell n is $2n^2$

Shell	n	Maximum number of electorns
K	1	$2 \times 1^2 = 2$
L	2	$2 \times 2^2 = 8$
M	3	$2 \times 3^2 = 18$
N	4	$2 \times 4^2 = 32$

The outermost shell of an atom, however, cannot have more than 8 electrons, except helium which has a pair of electrons only.

The electronic configurations of the inert gases are as follows :

Inert gases and their atomic number	Electrons in successive shells					
	Shell K n = 1	L 2	M 3	N 4	O 5	P 6
Helium 2	2					
Neon 10	2	8				
Argon 18	2	8	8			
Krypton 36	2	8	18	8		
Xenon 54	2	8	18	18	8	
Radon 86	2	8	18	32	18	8

As the charge on the positive nucleus is increased by one at each step an electron is added to the orbits, as the following illustrations clearly show.

An atom of hydrogen contains one proton in the nucleus and a single planetary electron in the first shell ; hence its atomic mass is one, and the atomic number is also one. The helium nucleus contains 2 neutrons and 2 protons—the planetary electrons are therefore two, all contained in the first shell. The next heavier element contains 4 neutrons and 3 protons in the nucleus—the planetary electrons being three only, 2 in the first shell and 1 in the second. The addition of electron in the second shell produces successively the elements lithium, beryllium, boron, carbon, nitrogen, oxygen, flourine and neon—with neon the second shell contains 8 electrons and is full. The next electron successsively enters the third shell unit it is full in argon—argon having 2 electrons in first shell, 8 in the second and 8 in third.

Atomic structure of first 20 elements in the Periodic Table

Element	Atomic weight	Atomic number	Electrons in orbits			
			K	L	M	N
H	1.008	1	1			
He	4.003	2	2			
Li	6.940	3	2	1		
Be	9.013	4	2	2		
B	10.820	5	2	3		
C	12.010	6	2	4		
N	14.008	7	2	5		
O	16.000	8	2	6		
F	19.000	9	2	7		
Ne	20.183	10	2	8		
Na	22.997	11	2	8	1	
Mg	24.32	12	2	8	2	
Al	26.98	13	2	8	3	
Si	28.09	14	2	8	4	
P	30.975	15	2	8	5	
S	32.066	16	2	8	6	
Cl	35.457	17	2	8	7	
A	39.944	18	2	8	8	
K	39.100	19	2	8	8	1
Ca	40.80	20	2	8	8	2

Electronic Theory of Valency.—Modern atomic structure largely explains the mechanisms of chemical changes. The elements helium, neon, argon, krypton, xenon and radion, are found to be inert chemically, i.e., they manifest no combining capacity, or what is called valency. Their chemical inertness is due to the stable electronic structure of their atoms.

The outermost shell of atoms of all the inert gases, except helium (which has two electrons only), contain eight electrons.

Chemical reactivity of other elements depends upon their tendency to assume the stable configuration of the inert gases so as to have an octet in the outermost orbit (or a duplet as in helium). This tendency may be satisfied either (a) by the *transfer* of electrons from one atom to another, or (b) by the *sharing* of electrons between two atoms, accordingly there are two main types of valency, viz., *electrovalency* and *covalency*. The electrons in outermost orbits are usually involved in chemical changes.

Electrovalency.—An examination of the atomic number shows that the inert gases are just *followed* by an alkali metal and *preceded* by a halogen. Metals in general follow the inert gases, while the non-metals precede them. The sequence is as follows :

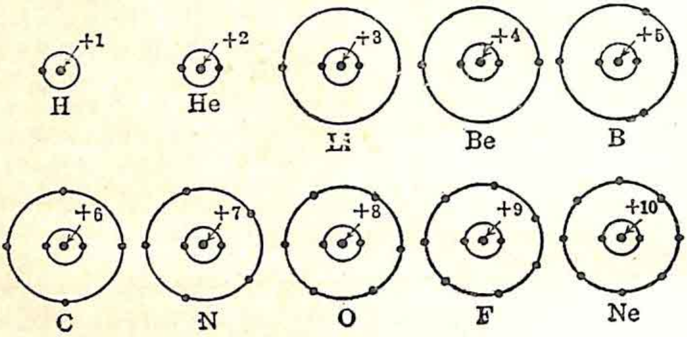


Fig. 36

	H	He	Li	
	1	2	2, 1	
O	F	Ne	Na	Mg
2, 6	2, 7	2, 8	2, 8, 1	2, 8, 2
S	Cl	A	K	Ca
2, 8, 6	2, 8, 7	2, 8, 8	2, 8, 8, 1	2, 8, 8, 2

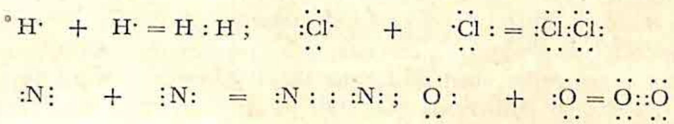
The combination between metals and non-metals, therefore, involves a process of electron transfer in which the surplus electrons of the metal supplies the deficit of electrons of the non-metal. Thus when an atom of sodium with one surplus electron combines with an atom of chlorine with a deficiency of one, producing common salt, sodium trasfers the surplus electron to chlorine and thereby satisfies their tendency to lose or gain electrons. The sodium atom has become positively charged owing to the loss of an electron and the chlorine atom negatively charged due to the gain of an electron. The electrically charged atoms, called ions, are then held together by electrostatic attraction, there being no definite bond between them. The ions come apart readily in solution or in the fused state and form independently mobile ions, and hence conduct electric current.

This type of valency which depends upon electron transfer is called *electro-valency*. It may be either *positive* or *negative* and is measured by the number of electrons a neutral atom *loses or gains* in the formation of the complete ocetet—a metal atom exhibiting positive electrovalency and the non-metals negative electrovalency. In common salt sodium has the positive electrovalency of one, and chlorine the negative electrovalency of one. In the formation of calcium chloride, and atom of calcium transfers its two surplus electrons to two atoms of chlorine—each accepting one electron ; hence calcium develops the positive electro-valency of two. In sodium sulphide two atoms of sodium—each having only one surplus electron—transfer 2 electrons to sulphur atom which has the deficit of two ; sulphur, therefore, has the negative electrovalency of two in this case. The electron transfer is illustrated by few examples.

Na	+	Cl			=	Na^+	+	Cl^-		
2, 8, 1		2, 8, 7				2, 8		2, 8, 8		
Cl	+	Ca	+	Cl	=	Cl^-	+	Ca^{++}	+	Cl^-
2, 8, 7		2, 8, 8, 2		2, 8, 7		2, 8, 8		2, 8, 8		2, 8, 8
Na	+	S	+	Na	=	Na^+	+	$S^=$	+	Na^+
2, 8, 1		2, 8, 6		2, 8, 1		2, 8		2, 8, 8		2, 8

Convalency.—The convalency consists in the mutual sharing of a pair of electrons between two atoms each of which has the deficit of electrons—of the shared pair each atom contributes one electron. Mutually shared electrons form a definite bond between the two atoms—the sharing of one, two or three pair giving rise to a single, double or a triple bond respectively. The atoms of non-metals which have the deficit of electrons combine with one another by covalency.

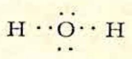
The diatomic molecules, H_2, Cl_2, O_2, N_2, etc., are formed in the following way—the electrons in the outermost orbit being shown only.



$$\mathrm{H\cdot + H\cdot = H:H}\;;\quad \mathrm{:\ddot{\underset{..}{Cl}}\cdot + \cdot\ddot{\underset{..}{Cl}}: = :\ddot{\underset{..}{Cl}}:\ddot{\underset{..}{Cl}}:}$$

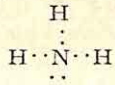
$$\mathrm{:N\vdots + \vdots N: = :N:::N:}\;;\quad \mathrm{\ddot{\underset{..}{O}}: + :\underset{..}{O} = \ddot{O}::\ddot{\underset{..}{O}}}$$

The formation of water, methane, ammonia, ethylene, acetylene and hydrogen chloride by covalent links is shown as follows :



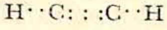
$\mathrm{H\cdot\cdot\ddot{\underset{..}{O}}\cdot\cdot H}$

Water



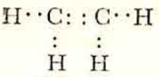
$\mathrm{H\cdot\cdot\overset{H}{\overset{\vdots}{\underset{..}{N}}}\cdot\cdot H}$

Ammonia



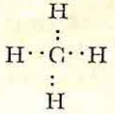
$\mathrm{H\cdot\cdot C:::C\cdot\cdot H}$

Acetylene



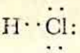
$\mathrm{H\cdot\cdot\underset{H}{\underset{\vdots}{C}}::\underset{H}{\underset{\vdots}{C}}\cdot\cdot H}$

Ethylene



$\mathrm{H\cdot\cdot\overset{H}{\overset{\vdots}{\underset{H}{\underset{\vdots}{C}}}}\cdot\cdot H}$

Methane



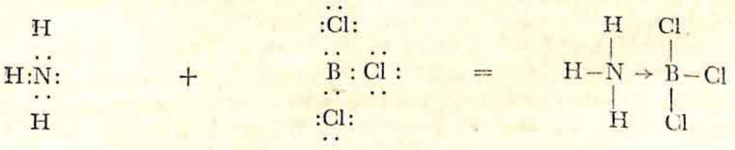
$\mathrm{H\cdot\cdot\ddot{\underset{..}{Cl}}:}$

Hydrogen chloride

The covalent link due to a shared pair of electrons gives rise to a definite bond between the atoms, while in electrovalent compounds the electrically charged atoms are held together by electrostatic attraction only—there being no bond in between them. This gives rise to difference between electrovalent and covalent compounds :

	Electrovalent compounds	**Covalent compounds**
(i)	Polar and conducts electricity when fused or dissolved.	Non-polar and non-conductors.
(ii)	Relatively high melting and boiling points.	Relatively low melting and boiling points, i.e., volatile.
(iii)	Usually insoluble in organic solvents, such as benzene.	Usually soluble in organic solvents.

Co-ordinate covalency—also called dative covalency, *semi-polar bond, or co-ordinate link.* The co-ordinate link is formed by the sharing of a pair of electrons, but the electrons are contributed by *one atom only*, and not by each atom as in covalency. Here one atom which contains a 'lone pair' of unshared electrons acts as the *donor*, while the other atom acts as the *acceptor*. Thus boron trichloride combines with ammonia—ammonia having a lone of pair of electrons and boron in boron trichloride having only 6 shared electrons in the outermost shell, which is 2 less than the octet. Here ammonia is the donor and boron trichloride the acceptor.



$$\mathrm{H:\overset{H}{\ddot{\underset{\underset{H}{..}}{N}}}:} + \mathrm{\overset{:\ddot{Cl}:}{\ddot{\underset{\underset{:\underset{..}{Cl}:}{..}}{B}}}:\ddot{\underset{..}{Cl}}:} = \mathrm{H-\overset{H}{\overset{|}{\underset{H}{\underset{|}{N}}}}\rightarrow\overset{Cl}{\overset{|}{\underset{Cl}{\underset{|}{B}}}}-Cl}$$

The co-ordinate link is represented by the arrow → with the head pointing towards the acceptor.

Isotopes and atomic number.—*The atoms of an element with different atomic masses but the same chemical properties are known as isotopes.*

Isotopes of an element have the *same atomic number* (i.e., the same number of protons in their nuclei) and hence the same chemical properties. The atomic number determines the planetary electrons in the orbits, and hence also the electrons in the outermost orbit (known as *valency electrons*), upon which depend the chemical properties of an element. *The atomic number is, therefore, the fundamental property of an element which determines its chemical property.* Isotopes are identical in all properties including the chemical properties, which depend on the atomic number, but differ in those physical properties, such as density, rates of diffusion, etc., which depend on mass. Isotopes (*isos*, equal and *topos*, place) occupy the same place in the periodic table.

It is the number of neutrons in the nucleus which makes the difference in the atomic masses of various isotopes of the same element and not the number of protons which is constant for all the isotopes of a given element—the number of neutrons varies in the different isotopes. Chlorine, for example, has two isotopes of atomic masses 35 and 37—one containing 17 protons and 18 neutrons in the nucleus while the other contains 17 protons and 20 neutrons only—the atomic number in each case being 17. The atomic mass of an isotope (also known as the *mass number*) which is the sum of the protons and neutrons in the nucleus is always a whole number, since protons and neutrons are particles of unit mass. The atomic weight of an element, as determined by chemical analysis, is but *an average of the atomic masses of various isotopes of an element as found in nature.*

Elements with fractional atomic weights exist as mixture of isotopes whose mass numbers have integral values.

Thus ordinary chlorine contains the two isotopes of atomic masses 35 and 37 in such a proportion that its average atomic mass is always found to be 35.457. Argon has three isotopes of atomic mass 40, 38 and 36 and its average atomic mass is 39.944. Potassium has three isotopes of atomic mass 39, 40 and 41, and its average atomic mass is 39.10. The atomic numbers of argon and potassium are 18 and 19 respectively, and hence quite correctly argon precedes potassium in the periodic table.

In the year 1869 the great Russian chemist Mendeleeff made a classification of elements on the basis of their atomic weights. He observed that the properties of elements depended on the magnitude of their atomic weights and enunciated the law that "*the physical and chemical properties of elements are periodic functions of their atomic weights.*"

On the basis of the above periodic law the elements were classified into several groups in a table (known as periodic table) in such a way that chemically related elements came in the same group, e.g., the alkali metals sodium, potassium, etc., were placed in group I, while the halogens fluorine, chlorine, bromine and iodine in group VII in the periodic table. The periodic classification of elements based on atomic weight is of great help in the systematic study of inorganic chemistry, but it is not without it defects, since the atomic weight is not a constant property of an element—the discovery of isotopes definitely establishing that there may be different atomic weights of the same element. The defects of the atomic weights-based classification disappear if the elements are classified in the order of their atomic numbers which really determine the chemical properties of elements. Mendeleeff's periodic law is therefore, restated as follows:

The properties of elements are periodic functions of their atomic numbers.

Atomic structure and atomic theory.—Modern atomic structure contradicts the assumptions of Daltons atomic theory.—(i) An atom is not indivisible, as Dalton assumed, since it itself consists of the fundamental particles, protons, neutrons and electrons. (ii) The discovery of isotopes indicates that the atomic weight of an element is not constant as was the assumption of Dalton. In the light of modern theory of the atom *an element may be defined as a substance which is composed of atoms with same atomic number i.e., with the same positive charge in the nucleus.*

But the most fundamental assumption of the atomic theory—that an atom is the unit of all chemical changes still holds good, in spite of its complex structure.

Exercises

1. Make a short note on the structure of atom.

2. Explain the terms : electron, neutron, atomic number and co-valency. The nucleus of an atom of an element consists of 12 neutrons and 11 protons. What is the atomic weight and electrovalency of the element ? Give the electronic structure of : (i) helium atom, (ii) carbon atom.

XI

OXYGEN, HYDROGEN AND WATER

Oxygen

Symbol O. Formula O_2. Atomic number 8. Atomic weight 16 by definition. M. Pt.—218°C. B. Pt.—183°C. Density. 1 litre at N.T.P. weighs 1.429 grams. Solubility, 1 litre of water at 0°C dissolves 48.9 c.c. of oxygen at 1 atmosphere.

History.—Oxygen was independently discovered by Scheele and Priestley in the year 1774. Pristley prepared it by heating the red oxide of mercury by focussing sun's rays thereon by means of a convex lens. But its importance in combustion and respiration was first clearly recognised by Lavoisier who also gave it the name oxygen.

Occurrence.—Oxygen is by far the most abundant of the elements. It occurs *free* in the atmosphere of which it forms about 21% by volume or 23% by weight. In the *combined state* it occurs in *water*, in nearly all *rocks*, in *plants* and in *animals*. It forms about 88.8% of water by weight or 36% *of the ocean*, and nearly 50% of the earth's crust.

✓ **Laboratory preparation.**—In the laboratory oxygen is usually prepared by heating a mixture of 5 parts of potassium chlorate, $KClO_3$, with 1 part of manganese dioxide, MnO_2. The mixture is taken in a hard glass test tube fitted with a cork through which passes a delivery tube the further end of which dips under water in a pneumatic trough. The test tube is clamped in a horizontal position with its cork-end inclined slightly downwards, fig. 36a.

The potassium chlorate alone decomposes on heating into potassium chloride and oxygen ; the manganese dioxide acts as a *catalyst.* The liberated oxygen gas is collected *by the displacement of water* as follows : A gas jar completely filled with water and closed with a greased cover glass, is inverted over water, in the trough ; while under water, the cover glass, is removed and the gas jar is placed on the shelf of the trough so that the delivery tube reaches the mouth of the jar through an opening in the shelf. Oxygen collects in the jar by the displacement of water. When the jar is full of the gas, its mouth is closed with a cover glass, while still under water, and it is then removed from the trough. Several jars of oxygen are similarly collected.

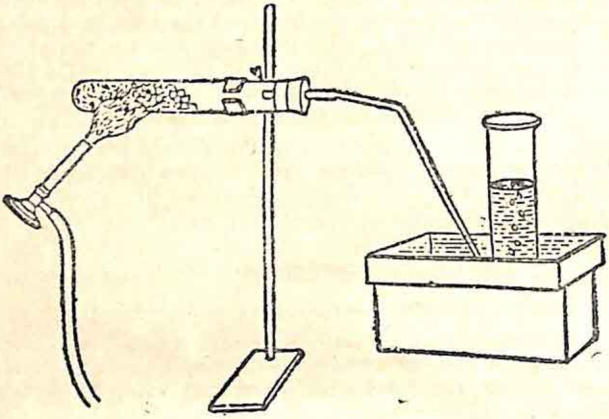


Fig. 36*a*

$2KClO_3$ (potassium chlorate) = $2KCl$ (potassium chloride) + $3O_2$.

When heated alone, potassium chlorate melts and rapidly gives off oxygen at 370° to 380°C—two reactions however taking place :

$$2KClO_3 = 2KCl+3O_2.$$
$$4KClO_3 = 3KClO_4 \text{ (potassium perchlorate) } + KCl.$$

Above 400°C the perchlorate also decomposes, liberating oxygen.

$$KClO_4 = KCl+2O_2.$$

In presence of a litte manganese dioxide potassium chlorate decomposes at less than 240°C. The manganese dioxide can be recovered unchanged in mass and composition at the end of the reaction, and hence acts merely as a catalyst, i.e., it simply helped the decomposition of potassium chlorate, but it has not undergone any permanent chemical change.

Manganese dioxide simply accelerates the decomposition of potassium chlorate.

This can be illustrated in a simple way. Two hard glass test tubes, one containing potassium chlorate alone, and another a mixture of manganese dioxide and potassium chlorate in the proportion of about 1 : 4, are embedded in sand in a sand-tray and heated. It will be seen that oxygen is evolved first from the tube containing the mixture.

Catalysis.—*Catalysis is a process in which the rate of a chemical reaction is altered (either increased or decreased) by the addition of a small quantity* *of a foreign substance which remains unchanged in mass and chemical composition at the end of the reaction—the added substance is known as the catalyst.*

A catalyst may accelerate or retard the reaction. When a catalyst increases the rate of reaction, it is called a *positive catalyst*, and the process *positive catalysis* ; e.g., manganese dioxide acts as a positive catalyst in the decomposition of potassium chlorate into potassium chloride and oxygen ; finely divided platinum catalyses the reaction of hydrogen with oxygen to give water, and activated charcoal the reaction of hydrogen with chlorine to yield hydrochloric acid.

When a catalyst diminishes the rate of a reaction, it acts as a *negative catalyst*, and the process is *negative catalysis*, e.g. phosphoric acid acts as a negative catalyst in retarding the decomposition of hydrogen peroxide into water and oxygen. Glycerine retards the oxidation of sodium sulphite to sodium sulphate by air.

Physical properties.—(i) Oxygen is a colourless, tasteless, and odourless gas which may be condensed to a pale blue liquid and frozen to a blue solid. Liquid and solid oxygen are strongly magnetic.

(ii) Oxygen is slightly soluble in water ; and hence the aquatic animals can live. Oxygen is, however, more soluble than nitrogen in water.

Chemical properties.—Oxygen is a very active element and readily combines with many elements (both metals and non-metals) and compounds, slowly at ordinary temperature and vigorously when heated evolving heat and light.

Combination of substances with oxygen, with evolution of heat and light, is known as combustion.

(i) Oxygen is a supporter of combustion but not combustible. Oxygen supports respiration and is essential to the life of plants and animals.

A glowing chip of wood is introduced into a jar of oxygen ; it is immediately *rekindled* but the gas does not burn.

(ii) **Combustion of non-metals in oxygen.**—Some non-metals such as carbon, sulphur, and phosphorus, burn in oxygen to form *acidic oxides*, i.e., oxides which dissolve in water to form acids.

(a) A piece of glowing charcoal taken in a deflagrating spoon is introduced into a jar of oxygen, the charcoal burns brilliantly, producing carbon dioxide. The contents of the jar are then shaken with water ; to a portion of the solution is added a few drops of blue litmus solution, it turns wine-red. The gas formed is, therefore, *a weak acid*. Clear lime water is added to the other portion, it turns milky owing to the formation of white insoluble calcium carbonate :

$C+O_2 = CO_2$; $CO_2+H_2O=H_2CO_3$ (carbonic acid)

$Ca(OH)_2$ (lime water) $+CO_2 = CaCO_3$ (calcium carbonate) $+H_2O$.

(b) Feebly burning sulphur, and phosphorus are similarly introduced into separate jars of oxygen ; sulphur burns with a bright bluish flame, producing sulphur dioxide, and phosphorus burns with a brilliant white flame, forming dense white cloud of phosphorus pentoxide. When shaken with water the products of combustion produce acids which turn blue litmus red.

$S+O_2 = SO_2$; $SO_2+H_2O = H_2SO_3$ (sulphurous acid).

$4P+5O_2 = 2P_2O_5$; $P_2O_5+H_2O = 2HPO_3$ (metaphosphoric acid).

$HPO_3+H_2O = H_3PO_4$ (orthophosphoric acid).

(iii) **Combustion of Metals in Oxygen.**—Some metals when heated burn in oxygen to give oxides. These are mostly *basic oxides,* i.e., oxides which react with acids to form salt and water.

(a) Small pieces of sodium and potassium are heated in deflagrating spoons until they begin to burn, and then introduced into jars of oxygen, they continue burning with bright yellow and violet flames respectively forming *peroxides* mainly which may be dissolved in water producing strongly alkaline solutions which turn red litmus blue :

$2Na + O_2 = Na_2O_2$ (sodium peroxide).

$2Na_2O_2 + 2H_2O = 4NaOH$ (sodium hydroxide) $+ O_2$.

$2K + 2O_2 = K_2O_4$ (potassium tetroxide).

$2K_2O_4 + 2H_2O = 4KOH$ (potassium hydroxide) $+ 3O_2$.

(b) Burning magnesium ribbon, inserted into a jar of oxygen, burns with a blinding white light, producing white solid magnesium oxide. A piece of iron wire tipped with burning sulphur and inserted in a jar of oxygen burns brilliantly, throwing off a shower of white-hot particles of ferroso-ferric oxide.

$2Mg + O_2 = 2MgO$ (magnesium oxide)

$3Fe+2O_2 = Fe_3O_4$ (ferroso-ferric oxide).

(iv) **At ordinary temperature.**—Oxygen combines fairly rapidly with the following reagents *in the cold.*

(a) Moist white phosphorus reacts with oxygen to yield phosphorus pentoxide—the reaction is used for removing *traces of* oxygen from inert gases such as nitrogen. Iron rusts in moist air, forming hydrated ferric oxide.

(b) a solution of potassium pyrogallate in caustic potash **absorbs** oxygen and turns black—the reaction is used in *gas analysis.*

(c) Nitric oxide combines with oxygen forming brown fumes of nitrogen dioxide—the reaction is used as a **test** for oxygen.

(d) Colourless solution of cuprous chloride in concentrated hydrochloric acid turns green on exposure to air due to formation of cupric chloride ; ammoniacal solution of cuprous chloride, however, turns blue in air.

$$4CuCl + 4HCl + O_2 = 4CuCl_2 + 2H_2O.$$

Test.—(i) Oxygen rekindles a glowing chip of wood.

(ii) Oxygen forms reddish brown fumes of nitrogen dioxide with nitric oxide : $2NO + O_2 = 2NO_2$.

Absorbents.—Oxygen is absorbed by : (i) a solution of potassium pyrogallate in caustic potash ; (ii) an acid solution of chromous chloride : '

$$4CrCl_2+4HCl+O_2 = 4CrCl_3+2H_2O.$$

Uses.—Oxygen is used (i) as an *aid to respiration* to patients suffering from breathing difficulties as in pneumonia and carbon monoxide poisoning ; in high altitude aviation ; in submarines ; tunnels, and montaineering, etc.

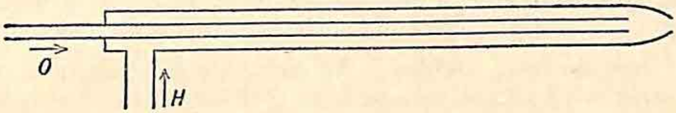


Fig. 37

(ii) in producing oxy-hydrogen and oxy-acetylene flames, much used for cutting and welding metals. An *oxy-hydrogen blowpipe* (fig. 37) consists of two *concentric* tubes ending in jets ; oxygen gas is passed through the inner tube and hydrogen through the outer,—the *mixture* when lighted at the jet produces an intensely hot, pointed flame (temperature about 2800°C) which readily melts platinum.

If the oxy-hydrogen flame impinges on a pencil of quick lime, an intensely white light, called *lime light* is emitted by the incandescent lime. In the *oxy-acetylene blowpipe*, acetylene gas takes the place of hydrogen ; a hotter flame, 3100°—3315°C, suitable for welding and cutting metals such as iron and steel, is obtained.

Liquid oxygen soaked in powdered charcoal has been used as an explosive.

Oxides.—*An oxide is a compound of two elements one of which is oxygen.* The oxides are classified as follows :

(i) **Basic oxides.**—A basic oxide is an oxide which reacts with an acid to yield a salt and water *only* :

MgO (magnesium oxide) $+2HCl = MgCl_2+H_2O$.

$CuO+H_2SO_4 = CuSO_4$ (copper sulphate) $+H_2O$.

Basic oxides are oxides of metals. If soluble in water they produce hydroxides which are also basic. Oxides of alkali metals (sodium, potassium, etc.) and alkaline earths (calcium, barium, etc.) dissolve in water forming soluble hydroxides (called *alkalis*) which turn red litmus blue.

$Na_2O+H_2O = 2NaOH$ (sodium hydroxide).

$CaO+H_2O = Ca(OH)_2$ (calcium hydroxide).

$2NaOH+H_2SO_4 = Na_2SO_4$ (sodium sulphate) $+2H_2O$.

$Ca(OH)_2+2HCl = CaCl_2$ (calcium chloride) $+2H_2O$.

(ii) **Acidic oxides.**—An acidic oxide is an oxide which reacts with a base to yield a salt. Carbon dioxide reacts with sodium hydroxide yielding sodium carbonate.

$CO_2+2NaOH = Na_2CO_3$ (sodium carbonate) $+H_2O$.

Sulphur dioxide yields sodium sulphite on treatment with caustic soda : $SO_2+2NaOH = Na_2SO_3$ (sodium sulphite) $+H_2O$.

An acidic oxide, if soluble, combines with water to yield an acid and it is, therefore, called *an acid anhydride*.

$P_2O_5+3H_2O=2H_3PO_4$ (phosphoric acid) ; $SO_3+H_2O=H_2SO_4$

An acidic oxide reacts with a basic oxide to yield a salt :

$CaO+CO_2=CaCO_3$ (calcium carbonate) ; $Na_2O+SO_3=Na_2SO_4$

Most of the oxides of non-metals (e.g., CO_2, SO_2, P_2O_5, etc.) and higher oxides of metals (e.g., CrO_3, Mn_2O_7 etc.) are acidic.

(iii) **Amphoteric oxides.**—An amphoteric oxide is one which acts as a weakly basic oxide towards a strong acid and a weakly acidic oxide towards a strong base, i.e., an amphoteric oxide, which is usually a metallic oxide, has both basic and acidic properties.

Zinc oxide reacts with hydrochloric acid to form zinc chloride and water, and hence behave as basic oxide ; but with sodium hydroxide it reacts as an acidic oxide forming sodium zincate :

Basic action : $ZnO + 2HCl = ZnCl_2 + H_2O$.

Acidic action : $ZnO + 2NaOH = Na_2ZnO_2$ (sodium zincate) $+ H_2O$.

Aluminium oxide, Al_2O_3 and stannous oxide, SnO, are also amphoteric.

(iv) **Neutral oxides.**—The oxides which are neither acidic nor basic in character are called neutral oxides ; e.g., carbon monoxide, CO ; nitrous oxide, N_2O ; and nitric oxide, NO.

(v) **Peroxides.**—A peroxide of an element contains more oxygen than what is present in its highest *typical acidic or basic oxide.* *A peroxide of a metal yileds hydrogen peroxide,* H_2O_2, *on treatment with cold dilute acids :*

Na_2O_2 (sodium peroxide) $+ 2HCl = H_2O_2 + 2NaCl$.

BaO_2 (barium peroxide) $+ H_2SO_4 = H_2O_2 + BaSO_4$.

A peroxide contains the oxygen chain—O—O—, as in sodium peroxide, Na—O—O—Na.

Metallic oxides such as lead dioxide, PbO_2 (usual basic oxide is PbO) and manganese dioxide, MnO_2 (usual basic oxide is MnO) which contain more oxygen than the basic oxides are not peroxides, since they do not yield hydrogen peroxide with dilute acids ; they are described as **poly-oxides.** They give oxygen with hot concentrated sulphuric acid, and chlorine with hot and strong hydrochloric acid :

$2MnO_2+2H_2SO_4 = 2MnSO_4$ (manganous sulphate) $+ 2H_2O + O_2$.

$MnO_2+4HCl = MnCl_2$ (manganous chloride) $+ 2H_2O + Cl_2$.

(vi) **Mixed oxides.**—A mixed oxide is formed by the combination of two simpler oxides. Thus ferroso-ferric oxide, Fe_3O_4, is a mixed oxide of the two basic oxides ferric oxide, Fe_2O_3 and ferrous oxide, FeO. It yields ferric and ferrous chlorides with hydrochloric acid.

$$Fe_3O_4(Fe_2O_3FeO)+8HCl = 2FeCl_3+FeCl_2+4H_2O.$$

Other reactions in which oxygen is liberated.—(i) Pure oxygen is evolved on dropping hydrogen peroxide solution into a solution of potassium permanganate in dilute sulphuric acid in the conical flask (fig. 38). The oxygen is collected over water ; the pink solution becomes solourless.

$$2KMnO_4+3H_2SO_4+5H_2O_2 = K_2SO_4+2MnSO_4+8H_2O+5O_2$$

(ii) Action of water on sodium peroxide also readily evolves oxygen :
$2Na_2O_2 + 2H_2O = 4NaOH + O_2$

(iii) Certain oxides of metals, many oxy-salts such as nitrates, and the oxy-acids such as sulphuric and nitric acid, decompose when heated, giving off oxygen.

$2HgO \rightleftharpoons 2Hg+O_2$;
$2BaO_2 \rightleftharpoons 2BaO+O_2$
$2Pb_3O_4 \rightleftharpoons 6PbO+O_2$;
$2PbO_2 = 2PbO+O_2$;
$4CrO_3 = 2Cr_2O_3+3O_2$;
$3MnO_2 = Mn_3O_4+O_2$;
$2KNO_3$ (potassium nitrate)
$= 2KNO_2$ (potassium nitrite) $+O_2$

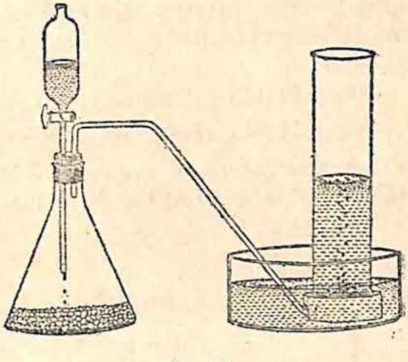


Fig. 38

$$2Pb(NO_3)_2 = 2PbO + 4NO_2 + O_2$$
$$2H_2SO_4 = 2H_2O + 2SO_2 + O_2$$
$$4HNO_3 = 2H_2O + 4NO_2 + O_2$$

Hydrogen

Atomic number 1. Atomic weight 1.008. Melting point --259°C. Boiling point −252.7°C. Density, 1 litre at 0°C and 760 mm. weighs 0.0899 gm. Solubility, 1 litre of water at 0°C dissolves 21.5 c.c. of the gas at 1 atmosphere.

History and occurrence.—Hydrogen was first prepared by Boyle in 1660 from iron filings and dilute mineral acids ; but it was carefully investigated by Cavendish in 1766 and called by him *inflammable air*. He also showed it to be a constituent of water (1781—84), a fact in virtue of which Lavoisier gave it the name *hydrogen* or 'water producer' in 1785.

In the free state hydrogen occurs in many volcanic and other natural gases, in the atmosphere of the sun, and in air in traces (about 1 part per million) only. In the combined state it is present in oils, fats, wood, coal, petroleum, water, etc.

Preparation.—The chief sources of hydrogen are—(i) *acids*, (ii) *water*, and (iii) *alkalis*.

Hydrogen from acids.—Hydrogen is obtained from acids by interaction with metals which are more electro-positive than hydrogen.

All the metals above hydrogen (with the exception of lead) in the electro-chemical series (only 13 metals have been mentioned here) displace hydrogen from acids, such as hydrochloric acid and sulphuric acid—the higher the metal in the series the more vigorous the displacement. The feebly electropositive metals like Cu, Hg, Ag, Au and Pt do not react.

Hydrogen is easily liberated by the action of dilute hydrochloric or sulphuric acid upon iron, magnesium and zinc or by the action of hot and strong hydrochloric acid upon tin :

K
Na
Ca
Mg
Al
Zn
Fe
Sn

$Fe+2HCl = FeCl_2$ (ferrous chloride) $+ H_2$,
$Fe+H_2SO_4 = FeSO_4$ (ferrous sulphate) $+ H_2$.
$Mg+H_2SO_4 = MgSO_4$ (magnesium sulphate) $+ H_2$,
$Sn+2HCl = SnCl_2$ (stannous chloride) $+ H_2$.

Pb
H
Cu
Hg
Ag
Au

Laboratory preparation.—Hydrogen is usually prepared in the laboratory by the action of dilute sulphuric acid (1 volume concentrated acid to 5 volumes water) or hydrochloric acid (1 volume concentrated acid to 2 volumes water) on granulated zinc :

$$Zn+2HCl \text{ (hydrochloric acid)} = ZnCl_2 \text{ (zinc chloride)} + H_2.$$

$$Zn+H_2SO_4 \text{ (sulphuric acid)} = ZnSO_4 \text{ (zinc sulphate)} + H_2.$$

A few pieces of granulated zinc are put under water in a two-necked *Woulfe's bottle* tightly fitted with corks through one of which passes a thistle funnel reaching down very nearly to the bottom and through the other passes the delivery tube which dips under water in a pneumatic trough (fig. 39). The apparatus must be perfectly **air-tight,** *since hydrogen forms an explosive mixture with air.* To test this, air is blown from the mouth through a rubber tube attached at the free end of the delivery tube when water is forced up the stem of the funnel. The apparatus is air-tight, if the water level in the funnel remain stationary after closing the rubber tubing by pressing hard with fingers.

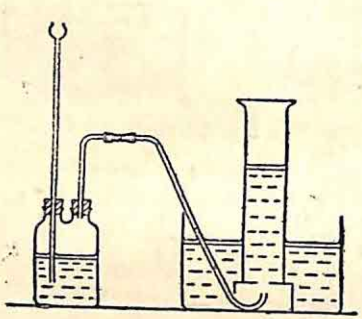


Fig. 39

Moderately strong sulphuric acid is then poured down the funnel, when a brisk reaction sets in with the rapid evolution of hydrogen. The gas is allowed to escape for a minute or two to drive out the air inside the bottle. To ensure this, a sample of the gas is collected in a test tube by the displacement of water and brought near the flame. When the gas burns *quietly*, it is free from air and is ready for collection. To collect the gas, a gas jar, completely filled with water and closed with a greased cover glass, is inverted over water in the trough ; while under water, the cover glass is removed and the gas jar is placed on the shelf of the trough so that the deilvery tube reaches the mouth of the jar through an opening in the shelf. Hydrogen collects in the jar *by the displacement of water*. When the jar is full of the gas, its mouth is closed with a glass plate, while still under water, and it is then removed from the trough. The jar is kept *with its mouth downwards.* Several jars of hydrogen are similarly collected to study its properties. The gas may be dried by passing through a U-tube containing calcium chloride or phosphorus pentoxide and collected over mercury.

Before collecting hydrogen all the air must be displaced from the apparatus, since hydrogen forms an explosive mixture with air

Physical properties.—(i) Hydrogen is a colourless, tasteless and odourless gas which is practically *insoluble* in water. The gas may be condensed only with difficulty to a liquid and frozen to a solid which *does not exhibit metallic properties.*

(ii) Hydrogen is the *lightest* of all substances. Air is 14.4 times heavier than hydrogen. The following experiments show that *hydrogen is lighter than air :*

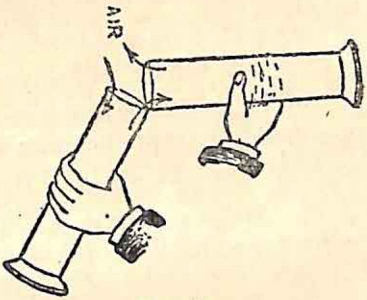


Fig. 40

Expt.—(a) An 'empty' gas jar (i.e., full of air) is inverted over a jar of hydrogen, and the cover glass from the mouth of the latter is then removed. After a few seconds when a lighted taper is applied to the mouth of the upper jar, it is found that the gas burns there with a slight explosion—hydrogen *being lighter than air has travelled to the upper jar* (fig. 40).

Expt.—(b) A toy rubber ballon is filled with hydrogen until it is sufficiently inflated ; it is then tied off with a loop of thread and released in air—the balloon rises up in the air.

Chemical properties.—(i) Hydrogen does not support combustion, but burns in air or oxygen with a pale blue non-luminous flame.

Expt.—A lighted taper is introduced into a jar of hydrogen, held mouth downwards —the taper is extinguished but the gas burns with a pale blue flame.

(ii) *Water is produced when hydrogen burns in air or oxygen.* This reaction is used as a *test* for hydrogen. $2H_2+O_2=2H_2O$.

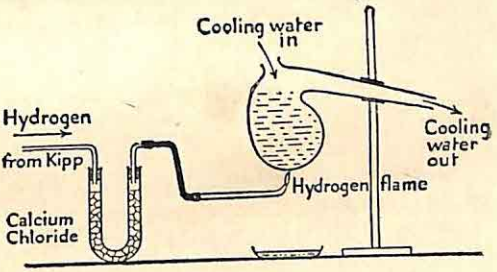


Fig. 41

Expt.—A stream of hydrogen, dried by passing through a U-tube containing fused calcium chloride, is burnt in a platinum jet, and the flame is allowed to impinge on the outer surface of a retort (fig. 41) through which cold water circulates. Drops of water condense on the cold outer surface and collect in a beaker placed below.

When glass tubes of different widths and lengths are lowered over the flame, a musical note is produced and the flame begins to sing.

(iii) *Hydrogen forms an explosive mixture with air or oxygen.*

Expt.—A soda water bottle is filled one-third its volume with oxygen and two-thirds by hydrogen, by displacement of water ; the bottle is wrapped with a towel, and well-shaken, and then held before a flame when a violent explosion takes place instantaneously.

(iv) *Hydrogen acts as a reducing agent*, because of its tendency to combine with oxygen.

Expt.—Hydrogen is passed over heated copper oxide taken in a bulbtube (fig. 42)—the *black* copper oxide is converted into metallic copper with *dull-red* colour and water is formed. Hydrogen here acts as a reducing agent, since it removes the oxygen from copper oxide—the removal of oxygen from a compound being called reduction.

$CuO + H_2 = Cu + H_2O$;

$PbO + H_2 = Pb + H_2O$.

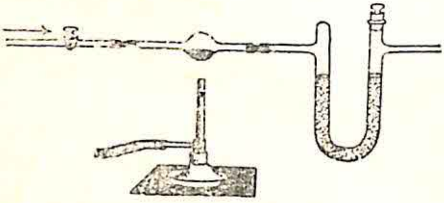


Fig. 42

(v) Hydrogen forms gaseous or volatile hydrides with all the non-metals, except the inert gases :

$$H_2+Cl_2 = 2HCl \; ; \quad 3H_2+N_2 = 2NH_3$$

(vi) Hydrogen forms solid *salt-like hydrides* with strongly electropositive metals like lithium, sodium, potassium, and calcium—the hydrides react with water producing hydrogen back :

$Ca+H_2 = CaH_2$ (calcium hydride) ; $2Na+H = 2NaH$.

$CaH_2+2H_2O = Ca(OH)_2$ (calcium hydroxide) $+2H_2$.

Calcium hydride is called hydrolith and is sometimes used to prepare hydrogen on a semi-technical scale.

Occlusion of hydrogen.—Hydrogen possesses the property of dissolving in certain metals forming *solid solution ;* the phenomenon is known as occlusion of hydrogen. Metals like iron, cobalt, platinum and specially palladium possess the property of absorbing a large volume of hydrogen at the ordinary temperature. Of all the metals, palladium absorbs hydrogen the most—about 900 times its own volume. The occluded hydrogen is released again when the metal is heated—use being made of this fact *in the purification of hydrogen.*

Occluded hydrogen is a powerful reducing agent. When *hydrogenised palladium,* for example, is immersed in a solution of ferric chloride, the latter is reduced to ferrous chloride.

Nascent hydrogen.—Nascent hydrogen is *hydrogen at the moment of its generation,* i.e., when it is just liberated from a compound. Nascent hydrogen is *more reactive and a more powerful reducing agent* than ordinary hydrogen, as the following experiments will show :

Expt.—(i) When zinc and sulphuric acid are added to *yellow* solution of ferric chloride, the latter is rapidly reduced to a *colourless* solution by the nascent hydrogen generated within it :

$FeCl_3$ (ferric chloride) $+ H = FeCl_2$ (ferrous chloride) $+ HCl$.

Expt.—(ii) When a little potassium permanganate, $KMnO_4$, solution is added to a mixture of zinc and sulphuric acid which is evolving hydrogen, the *pink* colour of the solution gradually disappears due to the reduction of the permanganate by nascent hydrogen ; but no change is produced when hydrogen is bubbled through the solution of potassium permanganate or ferric chloride.

$5Zn + 5H_2SO_4 = 5ZnSO_4 + 10H$ (nascent hydrogen)

By partial equations, $2KMnO_4 = K_2O + 2MnO + 5O$

$$K_2O + H_2SO_4 = K_2SO_4 + H_2O$$

$$2MnO + 2H_2SO_4 = 2MnSO_4 \text{ (manganous sulphate)} + 2H_2O$$

$$10H + 5O = 5H_2O$$

$$2KMnO_4 + 3H_2SO_4 + 10H = K_2SO_4 + 2MnSO_4 + 8H_2O$$

The nascent hydrogen is in the *atomic state* and hence its higher chemical reactivity.

Hydrogen from water.—Hydrogen may be obtained from water (i) *by electrolysis*, (ii) *by the action of metals*, and (iii) *by the action of carbon*.

(i) **Electrolysis of water.**—*Acidulated water is decomposed by electrolysis into* 2 *volumes of hydrogen and* 1 *volume of oxygen.*

(ii) **The action of metal upon water.**—Metals above hydrogen in the electro-chemical series, *except tin and lead*, decompose water, giving off hydrogen. The conditions under which water is decomposed by metals depend upon the nature of the metal. (a) **Action of metals upon cold water.**—Alkali metals (sodium, potassium, etc.) and the alkaline earth metals (calcium, strontium and barium) decompose water *at the ordinary temperature*, yielding hydrogen and the hydroxide of the metals which dissolve in the water.

The reaction with alkali metals is very violent ; it can be moderated by alloying the metal with lead or using an amalgam (alloy with mercury) of the metal.

When small pieces of sodium or potassium are thrown in cold water, they swirl about and gradually dissolve, giving off hydrogen ; in the case of potassium so much heat is generated that the evolved hydrogen ignites and a beautiful violet flame appears.

$$2Na + 2H_2O = 2NaOH \text{ (sodium hydroxide)} + H_2.$$

$$2K + 2H_2O = 2KOH \text{ (potassium hydroxide)} + H_2.$$

$$Ca + 2H_2O = Ca(OH)_2 \text{ (calcium hydroxide)} + H_2.$$

Expt.—To collect hydrogen from the reaction of sodium and water, the metal, in small pieces, is held under water with a wire gauze spoon, or pressed into a lead tube, and placed beneath an inverted jar of water. Hydrogen collects in the jar by the displacement of water. The water reacts alkaline *due to the solution of sodium hydroxide* produced in the reaction.

(b) **Action of metals upon boiling water.**—The metals magnesium and aluminium in the form of powder or as amalgam, and zinc coated with copper (since *pure zinc is not acted upon by water*) decompose boiling water, liberating hydrogen.

Amalgamated aluminium is made by rubbing aluminium foil with moist mercuric chloride. Zinc-copper couple is made by pouring copper sulphate solution over granulated zinc and washing the product free from adhering salts.

$$CuSO_4 + Zn = ZnSO_4 + Cu$$

$$Zn + 2H_2O = Zn(OH)_2 \text{ (zinc hydroxide)} + H_2.$$

$$2Al + 6H_2O = 2Al(OH)_3 \text{ (aluminium hydroxide)} + 3H_2.$$

Magnesium and aluminium amalgams also decompose cold water slowly.

(c) **Action of heated metals upon steam.**—Hydrogen is liberated when steam is passed over red-hot iron, zinc or magnesium. Magnesium burns brightly when heated in steam.

$$Mg + H_2O = MgO \text{ (magnesium oxide)} + H_2.$$

$Zn + H_2O = ZnO$ (zinc oxide) $+ H_2$.

$3Fe + 4H_2O \leftrightharpoons Fe_3O_4$ (ferroso-ferric oxide) $+ 4H_2$.

(iii) **Action of carbon on water.**—A mixture of carbon monoxide and hydrogen, (nearly in equal volumes), called **water gas,** is produced when steam is passed over white hot carbon heated to 1000°C—much carbon dioxide is produced at dull-red heat :

$C + 2H_2O = CO_2 + 2H_2$ *(dull-red heat)* ;

$C + H_2O = CO + H_2$ *(bright-red heat)*.

Hydrogen from alkalis.—Hydrogen may be obtained by heating the metals zinc, tin or aluminium, with 20 to 30 per cent caustic soda or potash solution in a flask—the gas may be collected over water.

$Zn + 2NaOH = Na_2ZnO_2$ (sodium zincate) $+ H_2$.

$2Al + 2NaOH + 2H_2O = 2NaAlO_2$ (sodium aluminate) $+ 3H_2$.

$Sn + 2NaOH = Na_2SnO_2$ (sodium stannite) $+ H_2$.

Tests for Hydrogen.—Hydrogen burns in oxygen with a pale blue flame to form water *only*—the product of combustion, i.e., water, does not make lime water milky, but turns *white* anhydrous copper sulphate *blue*.

Hydrogen is absorbed by spongy palladium which gives off the gas again on heating.

Uses.—Hydrogen is used industrially : (i) in the manufacture of ammonia, hydrochloric acid, and methyl alcohol ;

(ii) for hydrogenating petroleum fractions, and coal in order to obtain synthetic petrol ;

(iii) in the hydrogenation, also called *hardening*, of vegetable or animal oil—the oil combines with hydrogen in presence of finely divided nickel catalyst, forming solid fats, which are used extensively as butter substitutes :

(iv) in producing oxy-hydrogen flame, temperature about 2800°C, for welding and lime light—lead 'burning', i.e., autogenous welding without solder is done by a hydrogen flame ; a still hotter flame temperature about 4000°C, is produced in *atomic hydrogen* torches, also used for welding purposes.

(v) in filling air-ships and balloons, since it is the lightest gas known, its density relative to air = 1, is 0.069 only. For airships hydrogen is often replaced now-a-days by non-inflammable helium (having a lifting power of 92 per cent of that of hydrogen) as the inflammability of hydrogen makes its use extremely risky.

Pure Hydrogen.—(i) Hydrogen, obtained from commercial zinc and sulphuric acid contains many impurities, such as hydrogen sulphide, H_2S, arsine, AsH_3, phosphine, PH_3, sulphur dioxide, carbon dioxide, possibly oxides of nitrogen, nitrogen, and moisture. The gas is purified by passing it in succession through a series of U-tubes containing :

(a) lead nitrate solution to absorb hydrogen sulphide,

(b) silver sulphate solution to absorb arsine and phosphine,

(c) strong caustic potash solution to absorb sulphur dioxide, carbon dioxide, and nitrogen dioxide ;

(d) phosphorus pentoxide to absorb moisture.

The gas may be then collected over mercury. *To remove nitrogen*, the gas is passed in an evacuated glass bulb containing palladium foils which absorb hydrogen *only*—the nitrogen is pumped out of the bulb. Pure hydrogen is then evolved by heating the bulb to dull-redness.

The Kipp's apparatus.—To get a ready and fairly continuous supply of hydrogen for occasional use Kipp's apparatus (fig. 43) is conveniently used. It consists of two parts—(i) the lower part of two globes, the lowest being a half only, joined by a narrow neck, (ii) the upper part is another glass globe A with a long stem and fitting air-tight into the neck of the middle globe B,—the stem reaching nearly the bottom of the lowest globe. A stop-cock is attached to the central globe. The bottom globe C is provided with an outlet for the escape of the waste liquid.

Pieces of granulated zinc are placed in the central globe B. The stop-cock is opened and dilute sulphuric acid is poured in through a funnel down the upper globe until it fills the bottom globe C and comes in contact with the zinc in the central globe. The reaction takes place between the zinc and the acid. Hydrogen is evolved and passes out through the stop-cock.

When the gas is not required, the stop-cock is closed ; the evolved gas cannot pass out ; it collects in the central globe and exerts pressure on the acid liquid which is thereby forced down into the bottom globe whence it rises up the stem into the top globe. The contact between the zinc and the acid breaks and consequently the evolution of hydrogen ceases.

When the gas is wanted, the stop-cock is opened ; the accumulated gas escapes and so the pressure inside falls and the acid as a result comes down in contact with zinc again and the gas is evolved.

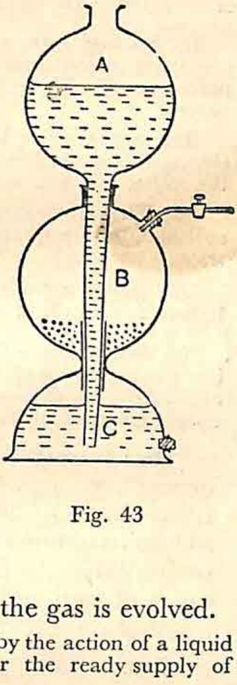


Fig. 43

The Kipp's apparatus is used whenever a gas is obtained by the action of a liquid upon a solid *without application of heat*—hence its use also for the ready supply of hydrogen sulphide, carbon dioxide, etc.

Water

Formula H_2O. Molecular weight 18. Freezes at 0°C and boils at 100°C at standard atmospheric pressure. Density at 4°C is unity. Critical temperature 365°C. Volume of 1 kilogram of water at 4°C is the standard litre ; it occupies 1000 ml.

History and Occurrence.—Water for a long time was regarded as an element —the elements, according to the ancient philosophers, being five in number only, namely, fire, air, earth, water and ether. It was only in the year 1781 that water was shown to be a compound by Cavendish who obtained it by exploding a mixture of hydrogen and oxygen in the ratio of 2 to 1 by volume.

Natural waters.—Natural waters contain many impurities—their nature and amounts varying with the source of water. Hence water may be classified according to their sources, as: (a) rain water, (b) river water, (c) spring and well water, (d) mineral waters, and (e) sea water.

(a) **Rain water.**—The purest form of natural water is rain *water*. It contains in solution the gaesous impurities oxygen, nitrogen and carbon dioxide absorbed from the atmosphere, and traces of ammonium nitrate, produced during thunderstorms, and common salt derived from dried sea spray carried inland by winds.

(b) **River water.**—Rain waters feed rivers. Hence the river water contains additional impurities dissolved out from the soil and rocks—the impurities frquently include the chlorides, sulphates, carbonates and bicarbonates of sodium, calcium, magnesium and iron.

The presence of soluble calcium and magnesium salts in river water makes it *hard*. The river water is often liable to be contaminated with the sewage and sludges of cities it flows by, and is then likely to contain organic matter, ammonia and nitrites.

(c) **Spring and well-water.**—The rain water, on reaching the ground, percolates through the porous starta of the soil—this natural filtration through the porous strata removes the suspended impurities but increases the soluble mineral content.

The spring water is usually hard and also free from organic matter, ammonia, etc., as they are oxidised by soil bacteria. Because of freedom from organic matter, the spring and well water is often suitable as drinking water.

(d) The spring water often contains an excess of mineral matter which confers a special taste or a specific curative and medical property to it ; it is known as *mineral water*.

Hot springs are often used for medicinal bath, they contain dissolved gases like helium and traces of radium emanation.

(e) **Sea water.**—Rivers carry a large volume of waters with dissolved impurities into the sea, and as such the sea contains the maximum amount of dissolved impurities, about 3.6% on the average, of which 2.6% is common salt. It is highly saline and unsuitable as drinking water and is hard.

Hard and soft waters.—Water is classed as hard or soft depending upon its behaviour towards soap solution. Water that really forms a lather of films and froths when agitated with a soap solution is known as *soft water*, while the water that reacts with the soap solution to form a white scum only without producing a lather easily, is said to be *hard water*—hard water does not, therefore, yield a lather until a considerable amount of soap has been used up.

The hardness of water is due to the presence of dissolved salts of metals (except the salts of alkali metals such as sodium and potassium), notably those of calcium, magnesium and iron, in water.

Ordinary soaps consist of sodium and potassium salts of certain fatty acids, such as salts of stearic acid, palmitic acid, and oleic acid derived from fats and oils ; they are soluble in water. When hard water is treated with a soap solution, the soluble sodium stearate (sodium stearate representing the soap) reacts with the calcium, magnesium and iron salts present in hard water to yield insoluble slimy precipitates of the stearates of calcium, magnesium and iron. Soap is thus removed from water.

$$\text{Na-stearate} + \text{Ca-salt} = \text{Ca-stearate} + \text{Na-salt}.$$

Hard water will not, therefore, form a lather with soap until sufficient has been added to precipitate all the calcium, magnesium and iron in the water as insoluble stearate. For convenience hardness is classified as *temporary* and *permanent*.

(i) **Temporary hardness.**—It is due to the presence of soluble *bicarbonates* of calcium, magnesium and iron in water. Temporary hardness can be removed by : (a) **boiling,** when the soluble bicarbonates are converted into insoluble carbonates which are precipitated, and carbon dioxide is evolved. The method is effective on a domestic scale only.

$$Ca(HCO_3)_2 = CaCO_3 + H_2O + CO_2\ ;$$
$$Mg(HCO_3)_2 = MgCO_3 + H_2O + CO_2.$$
$$Fe(HCO_3)_2 = FeCO_3 \text{ (ferrous carbonate)} + H_2O + CO_2.$$

Ferrous carbonate is readily oxidised by atmospheric oxygen, and reddish-brown ferric hydroxide is precipitated.

$$4FeCO_3 + 6H_2O + O_2 = 4Fe(OH)_3 + 4CO_2.$$

(b) **Clark's process.**—Temporarily hard water is *softened* by adding the *calculated* quantity of slaked lime which precipitates the insoluble carbonates which are filtered off.

$$Ca(HCO_3)_2 + Ca(OH)_2 = 2CaCO_3 + 2H_2O.$$
$$Mg(HCO_3)_2 + Ca(OH)_2 = MgCO_3 + CaCO_3 + 2H_2O.$$

The magnesium carbonate which is appreciably soluble, then reacts with further quantity of lime to form the insoluble magnesium hydroxide :

$$MgCO_3 + Ca(OH)_4 = Mg(OH)_2 + CaCO_3.$$

(ii) **Permanent hardness.**—This is caused by the presence of the chlorides and sulphates of calcium and magnesium in the water. Like the temporary hardness, permanent hardness can not be removed by mere boiling, or by adding lime, since such methods do not precipitate the calcium or magnesium.

Permanently hard water is softened by the addition of sodium carbonate to water, when insoluble calcium and magnesium carbonates precipitate. The sludges of the insoluble carbonates is removed by filtration through a filter press.

$$CaSO_4 + Na_2CO_3 = CaCO_3 + Na_2SO_4\ ;$$
$$MgCl_2 + Na_2CO_3 = MgCO_3 + 2Na_2Cl.$$

Water softening.—(a) **Lime-soda process.**—In softening hard waters for industrial purposes (for use in boilers and laundries) both the *temporary* and *permanent hardness* are removed simultaneously by adding *lime and washing soda* in correct proportion.

The lime and sodium carbonate precipitate the calcium and magnesium by reactions as stated above.

Magnesium chloride, if present, reacts with lime as follows :

$$MgCl_2 + Ca(OH)_2 = Mg(OH)_2 + CaCl_2.$$

The calcium chloride formed is then precipitated by sodium carbonate. $CaCl_2 + Na_2CO_3 = CaCO_3 + 2NaCl.$

The precipitate is allowed to settle and then removed by filtration.

(b) **The permutit process.**—This is an effective method of removing both temporary and permanent hardnesses of water. The permutit is the name for artificially prepared sodium aluminium silicate allied to the natural mineral *zeolite*.

The base exchange material permutit may be formulated at Na_2Ze, where Ze is the zeolite radical.

In the permutit process the hard water is allowed to percolate through a bed of granules of permutit, when the calcium and magnesium salts in the water react with the permutit forming insoluble calcium and magnesium aluminium silicates which are retained in the filter bed. The issuing water, free from calcium and magnesium, is soft.

$$Na_2Ze + Ca(HCO_3)_2 = CaZe + 2NaHCO_3$$
$$Na_2Ze + MgSO_4 = MgZe + Na_2SO_4.$$

The calcium and magnesium ions in the hard water are thus exchanged for an equivalent of sodium ions in the permutit and the hard water gets softened.

After use for some time when the permutit gets exhausted and loses its activity, it is regenerated by percolating with a 10 per cent solution of common salt—the sodium chloride displaces the calcium and magnesium from the exhausted permutit and replaces these by sodium, so that the bed is regenerated and ready for use again :

$$CaZe + 2NaCl \rightleftarrows CaCl_2 + Na_2Ze$$

Permutit water-softening plants are used in private houses and factories and also for softening public water supplies of towns.

Water for industrial purposes.—Soft water is used : (a) **in laundry,**—when hard water is treated with soap, the latter is removed from water as an insoluble precipitate and is not, therefore, available for detergent action until all the calcium and magnesium salts are removed, i.e., until the hard water is rendered soft.

Hard water, therefore, causes waste of soap, when used for laundry purposes, and hence the use of soft water for the same.

(b) **as boiler waters.**—Waters for raising steam in boilers must be soft so as to avoid the troubles of *scale formation*, and *corrosion*. The water must be soft as otherwise a deposit of calcium carbonate and calcium sulphate mainly is formed on the walls of the boiler. The formation of this hard, heat-insulating crust, called **boiler scale,** causes a much greater consumption of fuel, and also a rapid deterioration of the boiler due to overheating.

Properties of water.—(i) Pure water is a clear liquid, tasteless and colourless in small quantities but faintly blue when viewed in thickness. The m.p. of ice, 0°C, and the b.p. of water, 100°C, serve as the standard points in thermometry. Pure water is almost a non-conductor of electric current, since it is very slightly ionised into hydrogen and hydroxyl ions : $H_2O \rightleftarrows H^+ + OH'$; the conductivity is, however, increased by the addition of electrolytes.

(ii) Water is a stable exothermic compound : $2H_2 + O_2 = 2H_2O$ (steam) $+ 2 \times 58{,}000$ calories. It may be decomposed into its elements at a very high temperature (2000°C or above) by electric sparking or in contact with a white hot platinum. A mixture of hydrogen and oxygen in the ratio of 2 to 1 by volume, obtained by electrolysis, is known as **electrolytic gas.**

Water is decomposed by chlorine in presence of bright sunlight :

$$2H_2O + 2Cl_2 \rightleftharpoons 4HCl + O_2.$$

It may be decomposed by many metals and carbon, and also by electrolysis.

(iii) Water readily forms crystals of definite composition, called *hydrates* (p. 46), with many substances, e.g., oxalic acid, $C_2H_2O_4,2H_2O$; blue vitriol, $CuSO_4,5H_2O$—the combined water in these compounds is the water of crystallisation (p. 46).

(iv) Water is a good solvent, particularly for the acids, bases and salts. It dissolves acidic oxides yielding acids, and basic oxides producing hydroxides. Many substances undergo *hydrolysis* with water : $PCl_3 + 3H_2O = H_3PO_3$ (phosphorous acid) $+ 3HCl$.

(v) Trace of moisture is a necessary catalyst in many reactions.

(vi) The usual absorbents for moisture are fused $CaCl_2$, concentrated H_2SO_4, silicagel, P_2O_5 and magnesium perchlorate—of them the last two are the best.

Composition of water.—Water was first shown to be compound of hydrogen and oxygen by Cavendish in 1781. Electrolysis is a ready means of showing that water is made up of two volumes of hydrogen and one volume of oxygen.

Hofmann's experiment establishes the volumetric composition of steam. The experiment is carried out by sparking a certain volume of 2 : 1 hydrogen-oxygen mixture at a temperature *higher* than the condensing point of steam, 100°C, to obtain the volumetric relation between hydrogen and oxygen and the *steam* produced.

Cavendish was the first to show that water is formed by igniting a mixture of hydrogen and oxygen in the ratio of 2 to 1 by volume by means of an electric spark.

A mixture of 2 volumes of hydrogen and 1 volume of oxygen is introduced into the closed limb of a U-tube (fig. 44), by the displacement of mercury. The closed limb is covered with a wider tube through which passes the vapour of amyl alcohol boiling at 132°C. When the temperature has become steady, the volume of the gas mixture is noted by adjusting to equality the levels of mercury in the two limbs. The open limb is then closed firmly by the thumb and a spark is sent in the gas mixture from an induction coil, by means of platinum wires sealed at the top of the closed limb. There is an immediate contraction on sparking. The levels of mercury are again adjusted to equality after the explosion and the volume noted—it is two-third the original volume of the gas mixture.

The vapour of amyl alcohol is then cut off, when the temperature gradually falls below the condensing point of steam, (100°C) ; mercury slowly rises up and finally fills the closed limb completely—two-thirds the volume after explosion is, therefore, occupied by steam.

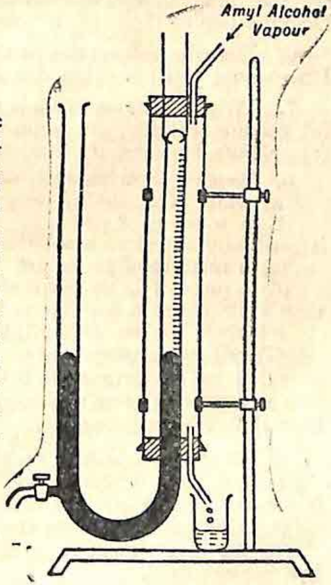


Fig. 44

Formula of steam.—From Hofmann's experiment it follows that : 2 vols. of hydrogen + 1 vol. of oxygen =2 vols. of steam.

By Avogadro's hypothesis, therefore.

2 mols. hydrogen+1 mol. oxygen = 2 mols. steam.

∴ 1 mol. hydrogen + $\frac{1}{2}$ mol. oxygen = 1 mol. steam.

∴ 2 atoms of hydrogen + 1 atom of oxygen = 1 mol. steam, since both hydrogen and oxygen molecules are diatomic.

∴ the molecular formula for steam is H_2O. Now, the vapour density of steam as found by experiment, is 9 and hence its molecular weight 18, which agrees with the formula H_2O for steam. (p. 70).

Exercises

1. How would you prepare a specimen of oxygen from potassium chlorate ? State its chief properties, tests and uses.

2. Outline briefly the characteristic properties of various classes of oxides. On what evidence is sodium peroxide classed as a peroxide, carbon dioxide as an acidic oxide, mercuric oxide as a basic oxide ?

3. Describe how you would prepare in the laboratory as pure a specimen of hydrogen as possible. What is meant by occluded hydrogen ? How would you show (a) that water is formed when hydrogen is burnt in air, and (b) that hydrogen is a reducing agent ? State its chief properties and uses. *P. U. Cal.* 1961

4. Describe methods for the preparation of hydrogen by the action of metals upon (a) cold water, (b) steam, (c) alkali and (d) a dilute acid. What is meant by nascent hydrogen ? Describe experiments to show that it is a more powerful reducing agent than ordinary hydrogen gas.

5. What is meant by hardness of water ? What is the hardness due to ? What are the disadvantages of hard water when used (a) in the laundry ; (b) in a boiler. Describe two methods of the removal of hardness of water.

6. Describe an experiment for determining the volumetric composition of steam. How would you therefrom deduce its molecular formula ? *Calcutta*, 1951.

7. Write equations to show the action of water upon the following substances—(a) calcium carbide, (b) sodium peroxide, (c) phosphorus pentoxide, (d) sodium, (e) calcium hydride, (f) iron, (g) magnesium, (h) zinc, (i) carbon.

8. Explain what happens when :

(a) water is added by drops on pellets of sodium peroxide.

(b) a solution of potassium permanganate acidified with dilute sulphuric acid, is gradually added to a solution of hydrogen peroxide.

(c) a mixture of potassium chlorate and manganese dioxide is heated.

(d) a piece of feebly burning phosphorus put into a jar of oxygen, and its contents then shaken with a few drops of blue litmus solution.

(e) air is shaken with alkaline pyrogallate in a tube.

(f) red oxide of mercury is strongly heated in a tube.

(g) a jar of nitric oxide is exposed to air.

(h) a glowing piece of charcoal is introduced into a jar of oxygen, and its contents then shaken with lime water.

(i) pellets of sodium are added to a dilute solution of caustic soda.

(j) hydrogen is passed over heated calcium, and the solid product that is formed, is treated with water.

(k) aluminium shavings are boiled with a 20 per cent solution of caustic soda.

(l) an iron pen-knife is dipped into a solution of ferric chloride containing hydrochloric acid.

(m) tin-foils are boiled with strong hydrochloric acid.

XII

OZONE AND HYDROGEN PEROXIDE

Ozone.—Ozone, O_3, is formed by the action of *silent electric discharge* upon pure and dry oxygen.

$$3O_2 \rightleftharpoons 2O_3$$

It is a deep blue gas with a *fishy smell.* Mercury loses its mobility in contact with ozone. It is slightly soluble in water but readily dissolves in *turpentine oil* which is an absorbent for the gas. It slowly decomposes at ordinary temperature and rapidily at 300° into oxygen. It is a powerful oxidising agent. Its molecular formula is O_3.

Allotropy.—Both oxygen and ozone contain the same element but they differ markedly in their properties. They are called *allotropes* —ozone is the allotropic modification of oxygen.

The property of an element to exist in different forms which differ more or less in their physical properties and to some extent in chemical properties is called allotropy.

Allotropy may be due to difference in the number of atoms in the molecule, as in the case of ozone and oxygen ; it may also be due to the difference in the arrangement of atoms in the molecule—the different allotropes, however, containing the *same* number of atoms in the molecule, as is found in the case of carbon and sulphur. Besides oxygen, carbon and sulphur, the elements phosphorus, silicon, tin, iron etc. also show allotropy.

The same solid substance, elementary or compound, may exist in different crystalline forms. This phenomenon is called **polymorphism.** The existence of red and yellow varieties of mercuric iodide, and the occurrence of silicon dioxide as quartz, sand, etc. are examples of polymorphism. Polymorphism in the case of an element is called allotropy—the term allotropy is, however, applied in the case of an element, be it solid, liquid or gaseous.

Different allotropes differ in their energy content. Rhombic sulphur, for example, is converted into monoclinic sulphur on heating, hence the latter contains more energy than the former.

Oxidation and Reduction

Oxidation.—The term oxidation is usually used to describe reactions which involve the addition of oxygen to a substance, such as the combustion of carbon into carbon dioxide the conversion of ferrous oxide into ferric oxide : *the electro-negative element oxygen is the oxidising agent in the above illustrations*

$$C+O_2=CO_2\ ;\ 4FeO+O_2=2Fe_2O_3.$$

Oxidation has, however, a much wider significance. Since oxygen is a typical electro-negative element, the term oxidation has been extended to include all reactions involving the addition of any electro-negative element or radical, such as sulphur, chlorine, sulphate radical, etc. Thus the conversion of ferrous and cuprous chlorides into ferric chloride and cupric chloride respectively, is regarded as typical oxidation reactions.

$$2FeCl_2+Cl_2 = 2FeCl_3\ ;\ \ 2CuCl+Cl_2 = 2CuCl_2$$

The ratio of the electro-negative or non-metallic to the electro-positive or metallic atoms or groups of a substance is, therefore, increased in oxidation. The removal of hydrogen or the metallic part i.e., the electro-positive atom or radical from a compound also increases the ratio. Therefore :

Oxidation is a reaction which involves (i) the addition or increasing the proportion of oxygen or any electro-negative element or radical to an element or a compound, or, (*ii*) *the removal or decreasing the proportion of hydrogen or any electro-positive element or radical from a compound.*

Illustrations.—(i) **Addition of oxygen.**—Heated in air or oxygen, rose-red copper is oxidised into black cupric oxide.

$$2Cu+O_2 = 2CuO \text{ (cupric oxide)}$$

(ii) **Addition of electro-negative element**—(a) Stannous chloride is oxidised to stannic chloride by the addition of chlorine ; Ferrous chloride is similarly oxidised to ferric chloride by chlorine :

$$SnCl_2+Cl_2 = SnCl_4\ ;\ \ 2FeCl_2+Cl_2 = 2FeCl_3$$

(b) Acidified solution of ferrous sulphate is oxidised to ferric sulphate by hydrogen peroxide—the sulphate radical is increased in proportion to the iron in the ferric sulphate.

$$2FeSO_4+H_2SO_4+H_2O_2 = Fe_2(SO_4)_3+2H_2O.$$

(iii) **Removal of hydrogen.**—Hydrochloric acid is oxidised to chlorine, when heated with manganese dioxide ; strong sulphuric acid liberates iodine from hydriodic acid ; ammonia can be oxidised to nitrogen by chlorine.

$$4HCl+MnO_2 = MnCl_2+2H_2O+Cl_2,$$

$$2HI+H_2SO_4 = SO_2+2H_2O+I_2\ ;\ 2NH_3+3Cl_2 = 6HCl+N_2.$$

(iv) **Removal of electro-positive element.**—Hydrogen peroxide liberates iodine from a solution of potassium iodide—potassium iodide is being oxidised to iodine : $H_2O_2+2KI = 2KOH+I_2$.

Reduction.—Reduction is the exact opposite of oxidation. The ratio of the metallic or electro-positive to the non-metallic or electro-negative atoms or groups of a substance is, therefore, increased in reduction. Therefore :

Reduction is a reaction which involves (i) *the addition or increasing the proportion of hydrogen or any electro-positive element or radical to an element or a compound, or* (ii) *the removal or decreasing the proportion of oxygen or any electro-negative element or radical from a compound.*

Illustrations.—(i) **Addition of hydrogen.**—Halogens are reduced to their hydracids by hydrogen sulphide and sulphur dioxide. Chlorine, for example, is reduced to hydrochloric acid by the addition of hydrogen, and sulphur precipitates when hydrogen sulphide is passed into chlorine water.

$$Cl_2+H_2S = 2HCl+S\ ;\quad Cl_2+SO_2+2H_2O = 2HCl+H_2SO_4$$

(ii) **Addition of electro-positive element.**—(a) Cupric chloride is reduced to cuprous chloride by nascent hydrogen or sulphur dioxide : $2CuCl_2+2H = Cu_2Cl_2+2HCl$.

$$2CuCl_2+SO_2+2H_2O = Cu_2Cl_2+H_2SO_4+2HCl.$$

On being heated with mercury, mercuric chloride is reduced to the mercurous chloride : $HgCl_2+Hg = Hg_2Cl_2$.

(b) White insoluble mercurous chloride is precipitated when stannous chloride is added to mercuric chloride solution :

$$2HgCl_2+SnCi_2 = Hg_2Cl_2+SnCl_4.$$

(iii) **Removal of oxygen.**—Hydrogen reduces heated copper oxide to metallic copper : $CuO+H_2 = Cu+H_2O$.

Aluminium powder reduces heated iron oxide to iron by the removal of oxygen : $Fe_2O_3+2Al = 2Fe+Al_2O_3$.

(iv) **Removal of electro-negative element or radical.**—Stannous chloride reduces a hot solution of ferric chloride to the ferrous state. Aluminium chloride is reduced to aluminium by heated sodium.

$$2FeCl_3+SnCl_2 = 2FeCl_2+SnCl_4\ ;\ AlCl_3+3Na = Al+3NaCl.$$

Ferric chloride (or sulphate) is reduced to the ferrous state by nascent hydrogen :

$$FeCl_3+H = FeCl_2+HCl\ ;\ Fe_2(SO_4)_3+2H = 2FeSO_4+H_2SO_4.$$

The process of oxidation and reduction always occur simultaneously—whenever one substance is oxidised, another substance must be correspondingly reduced, and *vice versa*. Thus, when carbon monoxide is passed over heated cupric oxide, copper and carbon dioxide are produced—carbon monoxide reduces copper oxide to metallic copper by the removal of oxygen, but is itself oxidised to carbon dioxide by taking up oxygen : $CuO+CO = Cu+CO_2$.

Sulphurous acid is oxidised to sulphuric acid by hydrogen peroxide but the latter itself is reduced to water by loss of oxygen :

$$H_2SO_3 + H_2O_2 = H_2SO_4 + H_2O.$$

Mercuric chloride is reduced to mercurous chloride by stannous chloride but stannous chloride is oxidised to stannic chloride by the addition of chlorine.

$$2HgCl_2 + SnCl_2 = Hg_2Cl_2 + SnCl_4.$$

An oxidising agent (also called an *oxidant*) is a substance which brings about the oxidation of another substance and itself gets reduced ; while **a reducing agent** (also known as *reductant*) is one which brings about the reduction of another substance but itself gets oxidised.

Valency change in oxidation and reduction.—*Oxidation and reduction reactions involve change of valency. The positive valency of an element is increased in the process of oxidation ; reduction is the decrease in the positive valency (or increase of negative valency).*

Thus when ferrous chloride is oxidised by chlorine into ferric chloride, the iron is oxidised, since its positive valency has increased from +2 to +3, whilst the oxidising agent chlorine is reduced, since its valency is changed from zero to −1 (chloride ion). *All free elements are taken of zero valency.*

During the reduction of ferric chloride by nascent hydrogen to the ferrous state, the positive valency of iron is decreased from +3 to +2, while the valency of hydrogen is changed from zero to +1 (in hydrochloric acid) and the latter is therefore oxidised :

$$2FeCl_2 + Cl_2 = 2FeCl_3 ; \quad FeCl_3 + H = FeCl_2 + HCl.$$

Electronic definitions of oxidation and reduction.—When ferrous chloride is oxidised by chlorine in aqueous solution :

$$2FeCl_2 + Cl_2 = 2FeCl_3$$

or, expressed ionically, $2Fe^{++} + Cl_2 = 2Fe^{+++} + 2Cl^-$, the ferrous ion Fe^{++} is converted into the ferric ion Fe^{+++} by the *loss of an electron* (oxidation) and the neutral chlorine into negatively charged chloride ion Cl^- by the *gain of an electron* (reduction), that is,

$$Fe^{++} - e = Fe^{++++} ; \quad Cl + e = Cl^-$$

Similarly, when ferric chloride is reduced by nascent hydrogen $FeCl_3 + H = FeCl_2 + HCl$ or expressed ionically, $Fe^{+++} + H = Fe^{++} + H^+$, the ferric ion Fe^{+++} gains an electron to be reduced to the ferrous ion Fe^{++}, whilst the reducing agent hydrogen loses the electron to be oxidised into the hydrogen ion H^+, that is,

$$Fe^{+++} + e = Fe^{++} ; \qquad H - e = H^+$$

This leads to the view that *oxidation is a process which involves the loss of one or more electrons by atoms or ions, whereas reduction is a process which results in the gain of one or more electrons by atoms or ions.*

An oxidising agent is one that gains electrons and is reduced to a lower valency state, while a reducing agent is one that loses electron and is oxidised to higher valency state. Thus the use of chlorine as an oxidising agent involves its reduction into chloride ion by the addition of electrons, while the use of sodium as a reducing agent is accompanied by its oxidation into sodium ion by loss of electrons : $Cl_2 + 2e = 2Cl^-$; $Na - e = Na^+$

In oxidation-reduction processes (or *redox processes*) electrons are transferred from the reducing agent to the oxidising agent.

Experiments to illustrate the processes of oxidation and reduction.—

(1) Stannous chloride solution is added by drops to a *hot yellow* solution of ferric chloride until just colourless—the ferric chloride is reduced to the ferrous state :

$$2FeCl_3 + SnCl_2 = 2FeCl_2 + SnCl_4.$$

(2) Stannous chloride solution is added gradually to a solution of mercuric chloride, when a white precipitate of mercurous chloride first forms, which finally turns grey due to its reduction to metallic mercury :

$$2HgCl_2 + SnCl_2 = Hg_2Cl_2 + SnCl_4 ; \quad Hg_2Cl_2 + SnCl_2 = 2Hg + SnCl_4.$$

(3) Potassium iodide solution is added to a solution of copper sulphate—a white precipitate of cuprous iodide is formed, which is coloured brown by iodine that is set free in the reaction :

$$2CuSO_4 + 4KI = 2K_2SO_4 + Cu_2I_2 + I_2.$$

Cupric copper (valency 2) has been reduced to the cuprous state (valency 1).

(4) Sulphur dioxide is bubbled through a green solution of cupric chloride solution when cuprous chloride is obtained as a *white* precipitate ; cupric chloride has been reduced to the cuprous state by sulphur dioxide :

$$2CuCl_2 + H_2SO_3 + H_2O = Cu_2Cl_2 + H_2SO_4 + 2HCl.$$

(5) A filter paper soaked in lead acetate solution is exposed to the action of hydrogen sulphide gas, when it turns *black* due to the formation of lead sulphide; the filter paper is again bleached *white* when dipped into a solution of hydrogen peroxide in a basin.

$$PbS + 4H_2O_2 = PbSO_4 + 4H_2O.$$

The lead sulphide is oxidised to lead sulphate which is white in colour.

(6) Potassium iodide is heated with strong sulphuric acid in a test tube, when *violet* vapours of iodine are evolved :

$$2KI + 2H_2SO_4 = 2KHSO_4 + 2HI; \quad 2HI + H_2SO_4 = 2H_2O + SO_2 + I_2.$$

(7) A piece of glowing charcoal is inserted in strong nitric acid in which it burns brilliantly—the carbon is oxidised to carbon dioxide by the nitric acid :

$$C + 4HNO_3 = CO_2 + 4NO_2 + 2H_2O.$$

Hydrogen peroxide H_2O_2

Hydrogen peroxide was discovered by Thenard in 1818. Hydrogen peroxide is prepared by the action of cold dilute mineral acids such as dilute sulphuric acid, upon a suitable metallic peroxide, such as barium peroxide, sodium peroxide, etc.

Laboratory preparation :—From barium peroxide : Finely ground barium peroxide is made into a paste of *hydrated* barium peroxide, $BaO_2, 8H_2O$, by treatment with water—anhydrous barium peroxide is not readily acted on by dilute sulphuric acid since the particles become coated with insoluble barium sulphate.

The paste is gradually added to *cold dilute* sulphuric acid (1 vol. of acid to 5 vols. of water) in a beaker cooled in crushed ice, stirring the mixture with a glass rod, until the solution is *just faintly acidic*—a trace of acid stabilises hydrogen peroxide. Barium peroxide reacts with sulphuric acid, forming hydrogen peroxide and a white precipitate of barium sulphate. The barium sulphate is allowed to settle and then filtered off—the filtrate is an aqueous solution of 10 to 20% hydrogen peroxide.

$$BaO_2+H_2SO_4 = BaSO_4+H_2O_2.$$

By passing carbon dioxide into a suspension of barium peroxide in water, barium carbonate is precipitated and a solution of hydrogen peroxide is formed—the barium carbonate is filtered off :

$$BaO_2 + H_2O + CO_2 = BaCO_3 + H_2O_2.$$

Commercial preparation.—(a) **From barium peroxide.**—Barium peroxide is hydrated by treatment with steam and the paste of hydrated barium peroxide is decomposed by cold dilute sulphuric acid, as in the laboratory process. But more recently it is decomposed by phosphoric acid.

$$3BaO_2 + 2H_3PO_4 = Ba_3(PO_4)_2 + 3H_2O_2.$$

The precipitated barium phosphate is filtered off, leaving a solution of hydrogen peroxide which is concentrated by distillation under reduced pressure.

The barium phosphate is decomposed by dilute sulphuric acid to liberate the phosphoric acid to be used again :

$$Ba_3(PO_4)_2 + 3H_2SO_4 = 3BaSO_4 + 2H_3PO_4.$$

The product obtained by this method is of better stability, since phosphoric acid acts as a preservative of hydrogen peroxide. The barium sulphate precipitate is used as a pigment extender under the name of **blanc fixe.**

(b) **From sodium peroxide.—Merck's process :** Calculated quantity of sodium peroxide is slowly added to ice-cold, dilute (20 per cent) sulphuric acid solution :

$$Na_2O_2 + H_2SO_4 = H_2O_2 + Na_2SO_4.$$

Most of the sodium sulphate separates on cooling as Glauber's salt $Na_2SO_4, 10H_2O$, and is filtered off. The filtrate, on distilling in vacuo, yields 30% solution of hydrogen peroxide, known as Merck's **perhydrol.**

(c) **From perdisulphuric acid.**—Hydrogen peroxide is obtained by electrolytic methods which involve the intermediate formation of perdisulphuric acid or its salts. Persulphuric acid is obtained by the electrolysis of ice-cold, 50 per cent sulphuric acid, using a platinum anode and a high current density ; this is hydrolysed with dilute sulphuric acid and the resulting hydrogen peroxide is distilled under reduced pressure. The hydrogen peroxide is obtained in pure 30 per cent solution.

It may be concentrated by distillation under low pressure upto about 90 per cent H_2O_2 which is *fairly stable.*

$$2H_2SO_4 = H_2S_2O_8 \text{ (perdisulphuric acid)} + H_2$$
$$H_2S_2O_8 + 2H_2O = 2H_2SO_4 + H_2O_2.$$

Pure Hydrogen peroxide.—The dilute aqueous solution of hydrogen peroxide is concentrated : (i) by evaporation in an open dish on a water bath, when the more volatile water vaporises away (b.p. of water 100°C ; that of hydrogen peroxide 151°C). The process is continued until the solution contains about 60 per cent hydrogen peroxide—further evaporation merely decomposes it into water and oxygen. (ii) by distillation under reduced pressure—the concentrated solution, on successive distillations under reduced pressure of 15 mm., yields hydrogen peroxide of 99 per cent purity.

Properties.—(i) Pure hydrogen peroxide is a colourless (in small amounts, but blue in bulk), syrupy liquid with the smell like that of nitric acid. It is soluble in water and ether. Its specific gravity is 1.46 at 0°. It freezes at—0.89°C. It decomposes explosively at its boiling point 151°C but may be distilled under reduced. pressure—it boils at 84°C under a pressure of 68 m.m.

Hydrogen peroxide yields *addition compounds* with some salts, e.g., $(NH_4)_2SO_4,H_2O_2$, and with urea, $CO(NH_2)_2,H_2O_2$—the hydrogen peroxide behaving like water of crystallisation. The addition compound with urea stabilised by citric acid, is known as *hyperol.*

(ii) **Stability.**—It slowly decomposes at the ordinary temperature, and readily when heated, forming water and oxygen and evolving much heat. $2H_2O_2 = 2H_2O + O_2 + 46{,}120$ calories.

The decomposition is promoted by many catalysts such as finely divided metals like gold and platinum black and certain solids such as manganese dioxide and the enzyme *catalase* which is present in milk and blood. The decomposition is also caused by *traces of alkali.* But small quantities of acid, namely phosphoric acid, calcium chloride, glycerine, etc. retard the deomposition, i.e., they act as negative catalysts, and are, therefore, used as preservatives for commercial hydrogen peroxide.

Colloidal platinum brings about a quick catalytic decomposition of hydrogen peroxide, yielding oxygen.

(iii) **Oxidising agent.**—It is a powerful oxidising agent ; thus :

(a) It liberates iodine from acidified potassium iodide—a reaction used for the estimation of hydrogen peroxide :

$$2KI + H_2O_2 + 2HCl = 2KCl + I_2 + 2H_2O.$$

(b) Lead sulphide is oxidised to lead sulphate :

$$PbS + 4H_2O_2 = PbSO_4 + 4H_2O.$$

The conversion of black lead sulphide into white lead sulphate is employed in restoring the colour of old oil-paintings which is tarnished due to the action of atmospheric hydrogen sulphide upon 'white lead' paints ; hence the use of hydrogen peroxide as a **bleaching agent.**

(c) Ferrous salts are oxidised to ferric salts in acid solutions :

$$2FeSO_4+H_2SO_4+H_2O_2 = Fe_2(SO_4)_3+2H_2O.$$

(d) It oxidises sulphurous acid to sulphuric acid, arsenious acid to arsenic acid, and hydrogen sulphide to sulphur and water :

H_3AsO_3 (arsenious acid) $+H_2O_2 = H_3AsO_4$ (arsenic acid) $+H_2O$.

$$H_2SO_3+H_2O_2 = H_2SO_4+H_2O \; ; \; H_2S+H_2O_2 = 2H_2O+S.$$

(iv) **Reducing property.**—It behaves as a reducing agent towards powerful oxidising agents, but strictly speaking, it is not a reducing agent, since it is itself reduced during the process :

(a) Potassium permanganate (*pink in colour*) in acid solution is rapidly reduced to a colourless solution :

$$2KMnO_4+3H_2SO_4+5H_2O_2 = K_2SO_4+2MnSO_4+8H_2O+5O_2.$$

(b) Silver oxide is reduced to metallic silver ; ozone is reduced to oxygen. Solutions of bleaching powder and sodium hypobromite liberate oxygen.

$$Ag_2O+H_2O_2 = 2Ag+H_2O+O_2 \; ; \quad O_3+H_2O_2 = H_2O+2O_2.$$

NaOBr (sodium hypobromite) $+H_2O_2 = NaBr+H_2O+O_2$.

(v) **Acid properties.**—Pure hydrogen peroxide has *feeble acidic properties*. It turns blue litmus red and reacts with barium hydroxide to give a precipitate of barium peroxide ; with sodium carbonate solution it yields carbon dioxide—oxygen is, however, evolved by the catalytic decomposition of H_2O_2, if the carbonate be in excess.

$$Ba(OH)_2+H_2O_2 = BaO_2+2H_2O \; ;$$
$$Na_2CO_3+H_2O_2 = Na_2O_2+H_2O+CO_2$$

Tests for hydrogen peroxide.—(i) Hydrogen peroxide liberates iodine from potassium iodide solution, which gives a blue colour with starch ; ozone also gives this reaction. But hydrogen peroxide *alone* readily liberates iodine potassium iodide *in presence of ferrous sulphate*.

(ii) A solution of potassium chromate acidified with dilute sulphuric acid is added to a dilute solution of hydrogen peroxide in a separating funnel. The solution is rapidly shaken with ether, which floats on the surface with a *deep blue colour*. This is the delicate 'perchromic acid' test for hydrogen peroxide, and is due to the formation of chromium peroxide, CrO_5, which is soluble in ether.

$$H_2CrO_4+2H_2O_2 = CrO_5+3H_2O.$$

(iii) Hydrogen peroxide is added to a *pink* solution of potassium permanganate acidified with dilute sulphuric acid—the pink colour is readily discharged, yielding a colourless solution.

(iv) Hydrogen peroxide is added to a solution of titanium dioxide in dilute sulphuric acid, an *orange yellow colour* develops due to the formation of titanium peroxide—a delicate test.

$TiO_2+H_2O_2 = TiO_3$(titanium peroxide)$.+H_2O$

The reagent is prepared by heating titanium dioxide TiO_2, with concentrated sulphuric acid, cooling and diluting with water.

Uses of Hydrogen Peroxide.—(i) As an oxidising agent in the laboratories ; Hydrogen peroxide in presence of ferrous sulphate (Fenton's reagent) is often used as an oxidising agent.

(ii) For restoring the colour of old oilpaintings containing white lead.

(iii) For bleaching the delicate fabrics like wool, silk, feather, ivory, etc., which would be injured by chlorine. Hydrogen peroxide bleaches hair to golden yellow colour.

(iv) As an antiseptic wash in surgery in dressing wounds. It is largely used as a gargle, spray and mouth-wash.

(v) As an *antichlor* to remove excess of chlorine from bleached fabrics :

$$H_2O_2 + Cl_2 = 2HCl + O_2.$$

(vi) 85 per cent solution of hydrogen peroxide had been used in Germany during the last war in the propelling charge of V-2 jet-propelled bombs—the hydrogen peroxide reacts with permanganates to give steam and oxygen for rocket propulsion. The concentrated hydrogen peroxide has also been used in burning fuels such as petrol, alcohol and hydrazine hydrate in producing power.

Strength of hydrogen peroxide solution.—It is stated in terms of volume of oxygen evolved on heating hydrogen peroxide solution. This is usually expressed in **'volume strength'** which means the c.c.'s of oxygen at N.T.P. that can be obtained from 1 c.c. of a sample of a solution of hydrogen peroxide.

$$\underset{68}{2H_2O_2} = 2H_2O + \underset{\text{22400 c.c. of oxygen at N.T.P.}}{O_2}$$

∴ 1 gm. of hydrogen peroxide gives 329.4 c.c. of O_2 at N.T.P.

Or 100 c.c. of 1 per cent solution gives 329.4 c.c. of O_2 at N.T.P.

∴ 1 c.c. of 1% solution of H_2O_2 gives 3.294 c.c. of O_2 at N.T.P.

1% solution of hydrogen peroxide, therefore, is of '3.294 volume' strength.

10 volume hydrogen peroxide is of 3.04 per cent strength ; 100 volume hydrogen peroxide is of 30 per cent strength.

A sample of hydrogen peroxide of 'v volume' strength is v/3.294 per cent solution.

Exercises

1. Explain what is meant by the term allotropy. Illustrate your answer with reference to oxygen, carbon and sulphur. *Calcutta* 1954.

2. Describe the preparation of an aqueous solution of hydrogen peroxide. What are its chief properties, tests and uses ? How does hydrogen peroxide react with (i) acidified potassium iodide, (ii) lead sulphide, (iii) silver oxide, (iv) ozone, and (v) acidified potassium permanganate, (vi) sulphrous acid ? Explain what is meant by '10 volume' hydrogen peroxide. *Calcutta* '53.

3. Explain what happens when :

(i) hydrogen peroxide solution is shaken with platinum black ;

(ii) hydrogen peroxide is added to a solution of sodium carbonate ;

(iii) a lead acetate paper is exposed to the action of hydrogen sulphide, and then steeped into hydrogen peroxide solution ;

(iv) a solution of ferrous sulphate containing a little dilute sulphuric acid is treated with hydrogen peroxide ;

(v) carbon dioxide is passed into a suspension of barium peroxide in water.

4. Explain clearly the terms oxidation and reduction. Illustrate your answer with experiments involving the use of : chlorine, hydrogen sulphide, sulphur dioxide, nitric acid, stannous chloride, and hydrogen peroxide. Discuss why a process of oxidation is always attended with that of reduction and *vice versa*.

P.U. 1961.

XIII

NITROGEN AND THE ATMOSPHERE

Nitrogen

Formula N_2. Atomic number 7. Atomic weight 14.008. Boiling point —195.8°C. Melting point—209.86°C. Solubility, 1 litre of water dissolves 23.5 c.c. at 0°C and 1 atmosphere.

History and Occurrence.—Nitrogen was discovered by Daniel Rutherford, but its true nature was first shown by Lavoisier (1775-76), who called it *azote*, as it did not support life, (*a*, no ; *zeo*, life). It was given the name nitrogen because of its presence in nitre.

In the free state it occurs in the atmosphere to the extent of 78% by volume. In combination it is present in plants and animals, mainly as proteins. It is also found as **nitre,** also called **salt petre,** KNO_3, and as **Chile salt petre**, $NaNO_3$, in desert soils in Chile.

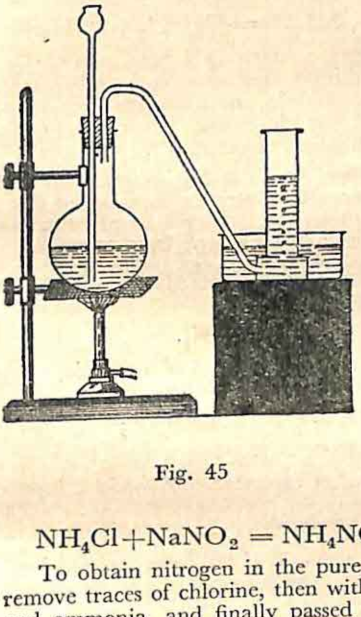


Fig. 45

Laboratory preparation.—Nitrogen is prepared in the laboratory by *gently* heating a solution of *ammonium nitrite.* Instead of ammonium nitrite, a concentrated solution containing equimolecular quantities of ammonium chloride and sodium nitrite is generally used. The solution is taken in a round bottomed flask (fig. 45) fitted with a thistle funnel and a delivery tube which dips under water in a trough, and is *gently* heated. Ammonium chloride reacts with sodium nitrite producing ammonium nitrite and sodium chloride ; the ammonium nitrite thus formed decomposes on heating into water and nitrogen which is collected by the displacement of water.

$$NH_4Cl+NaNO_2 = NH_4NO_2+NaCl\ ; \quad NH_4NO_2 = N_2+2H_2O.$$

To obtain nitrogen in the pure condition, the gas is first washed with alkali to remove traces of chlorine, then with concentrated sulphuric acid to absorb moisture and ammonia, and finally passed over heated copper filings to reduce oxides of nitrogen, and then collected over mercury.

Properties.—(i) A colourless gas without any smell or taste, nitrogen is very slightly soluble in water.

(ii) It does neither burn nor support burning. It does not turn lime water milky (*cf. carbon dioxide*). Though non-poisonous, the gas does not support respiration.

(iii) Rather inert at ordinary temperature, it enters into combination with many substances at higher temperature.

(a) *Combination with hydrogen.*—Under the influence of electric sparks nitrogen combines with hydrogen, forming ammonia. On a technical scale, they are made to combine together under a pressure of 200 atmospheres and in presence of an iron catalyst at a temperature of 550°C. $N_2+3H_2 \rightleftharpoons 2NH_3$.

(b) *Combination with oxygen.*—Under the influence of electric sparks at a high temperature of 3000°C nitrogen combines with oxygen to produce nitric oxide. $N_2+O_2 \rightleftharpoons 2NO$.

(c) *Combination with metals.*—Nitrogen is absorbed by red-hot metals like calcium, magnesium and aluminium, forming nitrides. A metallic nitride on hydrolysis yields a metallic hydroxide and ammonia :

$$3Ca+N_2 = Ca_3N_2 \;;\; Ca_3N_2+6HOH = 2NH_3+3Ca(OH)_2,$$
$$3Mg+N_2 = Mg_3N_2 \;;\; Mg_3N_2+6HOH = 2NH_3+3Mg(OH)_2.$$

(d) Nitrogen is absorbed by heated (1000°C) calcium carbide giving calcium cyanamide, NCaCN, technically called **nitrolim,** which is decomposed by steam, yielding ammonia.

$$CaC_2+N_2 = NCaCN+C \;;\; NCaCN+3H_2O = CaCO_3+2NH_3.$$

Uses of Nitrogen.—(i) Atmospheric nitrogen is fixed in large quantities as ammonia, nitric acid and nitrolim. (ii) Liquid nitrogen is a refrigerant. (iii) Nitrogen provides an inert atmosphere in certain metallurgical operations. (iv) In making gas thermometers and for filling electric bulbs. On a commercial scale nitrogen is obtained by the fractional distillation of liquid air.

Detection.—An inert gas, nitrogen is recognised by its lack of response to tests for the reactive gases. Like carbon dioxide, it does neither burn nor support burning ; but it is without action upon lime water. Nitrogen can however be absorbed by heated magnesium and can thus be distinguished and separated from argon.

Nitrogen (i) **from ammonia.**—Nitrogen may be prepared by warming a paste of bleaching powder with a solution of ammonia.

$$3Ca(OCl)Cl + 2NH_3 = 3CaCl_2 + 3H_2O + N_2.$$

It may be obtained by passing chlorine into a strong solution of ammonia, when ammonium chloride and nitrogen are formed :

$$2NH_3 + 3Cl_2 = N_2 + 6HCl \;;\; 6NH_3 + 6HCl = 6NH_4Cl \;;$$
$$\therefore\; 8NH_3 + 3Cl_2 = 6NH_4Cl + N_2$$

Ammonia must be in large excess, otherwise an explosive oily liquid, nitrogen trichloride, NCl_3, may be produced.

$$NH_3 + 3Cl_2 = NCl_3 + 3HCl.$$

(ii) **from nitric acid.**—Moderately dilute nitric acid (1 vol. conc. acid to 1 vol. water) reacts with copper turnings evolving nitric oxide, which when passed over heated copper filings yields nitrogen.

$$3Cu + 8HNO_3 = 3Cu(NO_3)_2 + 2NO + 4H_2O.$$
$$2NO + 2Cu = 2CuO + N_2.$$

(iii) **from air.**—Besides traces of moisture and carbon dioxide (about 0.04 per cent by volume), air is principally a mixture of nitrogen, oxygen and argon, roughly in the proportion of 78:21:1 by volume. Nitrogen may be obtained from air by removing the oxygen **by red-hot copper.** Carbon dioxide and moisture are first removed by passing the air through strong caustic potash solution and concentrated sulphuric acid in succession. The purified air is then passed through a long tube containing red-hot copper filings which fix the oxygen as oxide of copper and nitrogen passes out ; the gas may be collected over water :

$$2Cu + O_2 = 2CuO.$$

Nitrogen, thus obtained form air, contains about 1 per cent argon.

The Atmosphere

One litre of air at N.T.P. weighs 1.293 *gms. Density of air* ($H=1$) *is* 14.44.

Constituents of Air.—Air was regarded as an element by the ancient philosophers. The discovery of oxygen and nitrogen in air by Priestley and Scheele in 1774 led Lavoisier to establish in 1775 that air was a mixture of these two gases with traces of water vapour and carbon dioxide. Besides these gases, air contains the inert gases helium, neon, argon, krypton and xenon, discovered by Raleigh and Ramsay in 1894. Ozone, ammonia, nitric and nitrous acids, sulphur dioxide, dust particles, etc. also are present in air in minute traces.

The average percentage composition of ordinary air by volume is : nitrogen 77.16 ; oxygen 20.60 ; water vapour 1.40 ; argon and other inert gases 0.80 ; carbon dioxide 0.04.

The average composition of air, freed from moisture and carbon dioxide, is :

	By volume	By weight
Nitrogen	78.06	75.5
Oxygen	21.00	23.2
Inert gases	0.94	1.3

Air is a mixture.—That air is a mixture and not a compound of nitrogen and oxygen is evident from the following facts :

(i) The composition of air, freed from moisture and carbon dioxide is *nearly* but not *entirely constant*—slight variation in the proportion of nitrogen and oxygen in air is observed in different localities and at different times. The composition of a compound, on the other hand, is definitely *fixed and invariable.*

Percentage of oxygen by volume in air in : Berlin 20.960—20.973 ; Paris 20.913—20.999 ; Calcutta 20.105—20.385.

(ii) There is *no thermal change* nor is there any volume change when nitrogen and oxygen are mixed together in the proportion as they are present in air and the mixture behaves like ordinary air, while an accompanying heat change and often a volume change occur in chemical reactions between gases.

(iii) The properties of air are those of a mixture of nitrogen and oxygen, i.e., the properties of the components of air are additive, as obtains in a mixture. Moreover a mixture of nitrogen and oxygen, if made in the proportion as they are present in air, shows all the prperties of ordinary air.

(iv) If air were a compound, its molecular formula, as deduced from the percentage composition, would have been $N_{15}O_4$ (or a multiple of this) and hence its vapour density is 137.

The percentages of nitrogen and oxygen by weight in air are 75.5 and 23.2 respectively and hence the ratio of

$$\frac{\text{atoms of nitrogen}}{\text{atoms of oxygen}}=\frac{75.5/14}{23.2/16}=\frac{5.393}{1.450}=\frac{15}{4}$$

$\therefore$ the simplest formula for air is $N_{15}O_4$.

But it is actually found by experiments to be 14.4, which corresponds to a mixture of nearly 4 volumes of nitrogen and 1 volume of oxygen thus : $100\times d = 80\times 14+20\times 16$;

$$\therefore\ d = 14.4, \text{ where } d = \text{density of air } (\mathrm{H} = 1).$$

(v) The composition of air may be altered and its constituents partially separated by physical means, such as (a) *diffusion* and (b) *solution in water* : This is characteristic of a mixture only—a compound would diffuse or dissolve as a whole.

(a) When air is allowed to diffuse through a porous membrane of unglazed porcelain, nitrogen, being lighter than oxygen, passes out more rapidly than oxygen, causing a partial separation of the constituents of air.

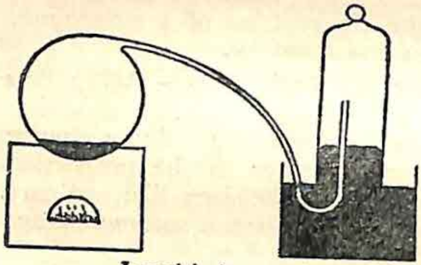
(b) When air is shaken with water, the dissolved air becomes richer in oxygen than the undissolved air, since oxygen is more soluble in water than nitrogen.

The dissolved air expelled by boiling the water contains nitrogen and oxygen approximately in the ratio of 2 : 1 by volume, as against 4 : 1 in normal air.

(vi) The constituents of air may be separated by the fractional distillation of liquid air. A compound would distil as a whole.

Volumetric composition of air.—Lavoisier's experiment.— The composition of air by volume was determined by the French savant Lavoisier (1743—1794) by his classical experiments on calcination of mercury in air which he began in 1775—76. Lavoisier carried out the following famous experiment in 1775—1776.

Lavoisier heated a weighed quantity (about 4 oz.) of mercury in a glass retort the neck of which communicated with a measured volume of air in a bell-jar standing over mercury (fig. 46). Red scales (mercuric oxide) were formed and found floating on the surface of mercury in the retort and the level of mercury gradually rose up in the bell-jar during heating —the level became steady after 12 days. The residual air in the bell-jar occupied four-fifths the total volume of air taken. The residual air did not support life or combustion. It was called **azote** (*a*, no *zoe*, life) by Lavoisier.



Lavoisier's experiment

Fig. 46

The red scales of mercury were collected, weighed and heated very strongly in a retort when a gas was liberated—its volume being equal to one-fifth that of the original air in the apparatus and was exactly equal to the diminution in volume of the air in the first experiment.

This gas supported life and combustion ; it was called **oxygen** by Lavoisier. When this gas was mixed with azote (residual air) ordinary air was obtained. From these two experiments Lavoisier concluded that :

(i) air is a mixture of two gases, azote (nitrogen) and oxygen, in the approximate ratio of 4 : 1 by volume.

(ii) Oxygen of air alone supports combustion and respiration.

Ammonia NH_3

Vapour density 8.5. Boiling point −33.4°. Melting point −77.7°. Critical temperature 132.5°.

Occurrence.—Ammonia is a product of the decomposition of organic matter, containing nitrogen. The stable manure, for example, contains urea, $CO(NH_2)_2$, derived from the urine of animals. The urea is converted by the action of bacteria into ammonium carbonate which slowly decomposes, yielding ammonia, and hence its smell in a stable, and its presence in traces in air.

$$CO(NH_2)_2 + 2H_2O = (NH_4)_2CO_3 \; ; \; (NH_4)_2CO_3 = 2NH_3 + H_2O + CO_2.$$

Laboratory preparation.—Ammonia is prepared by the action of a strong base, such as lime or caustic soda, upon ammonium salt. An intimate mixture of ammonium chloride (1 part) and dry slaked lime (3 parts) is used in the laboratory. The mixture is heated in a flask or a hard glass test-tube (fig. 47)—the evolved ammonia is dried by passing through a tower filled with lumps of quick lime and then collected in gas jars by the *downward* displacement of air or over mercury :

$$2NH_4Cl + Ca(OH)_2 = CaCl_2 + 2NH_3 + 2H_2O.$$

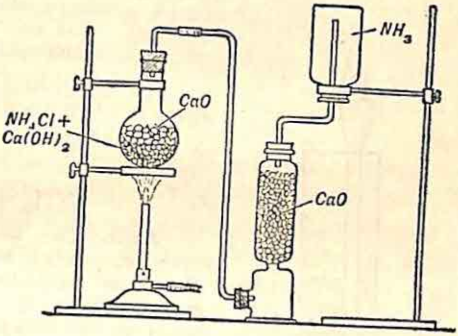


Fig. 47

Drying of ammonia.—The gas cannot be dried by strong sulphuric acid or phosphorus pentoxide which itself absorbs ammonia that is basic, yielding ammonium sulphate or phosphate. Calcium chloride also absorbs the gas forming a compound $CaCl_2, 8NH_3$ and hence also unsuitable as a drying agent. **Ammonia is dried by quick lime which itself is basic.**

A supply of ammonia is readily obtained in the laboratory by allowing liquor ammonia to fall in drops from a dropping funnel into a flask containing solid sticks of caustic soda.

Properties.—(i) Ammonia is a colourless gas with a pungent smell (odour of smelling-salt) and is *lighter than air.* The gas is readily liquefied by pressure alone (6 atmospheres at 10°).

Expt.—An *empty* jar (i.e., containing air) is inverted over a jar of ammonia and the lid is removed. Ammonia, being lighter than air, travels in the upper jar—tested by introducing a glass rod moistened with concentrated hydrochloric acid when dense white fumes of ammonium chloride are evolved.

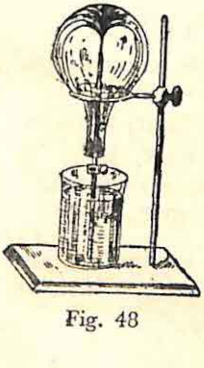


Fig. 48

(ii) It is the most soluble of all gases—1 volume of water at 0°C dissolves 1150 volumes of ammonia to give a solution containing 47% ammonia by weight. A saturated solution of sp. gr. 0.88 contains only 35% ammonia. The concentrated solution is known as **liquor ammonia fortis.** *A bottle of liquor ammonia* *should be carefully opened after cooling in ice, as there is always a high pressure inside.*

The solution of ammonia is alkaline to litmus. The solubility in water and the alkalinity of the solution are shown by the *fountain experiment :*

Fountain experiment.—A round bottomed flask (fig. 48) is filled with dry ammonia and closed with a cork through which passes a long tube provided with a stop cock—one end of the tube drawn into a jet, is inside the flask and the other dips in red litmus solution. The stop cock is opened and a little ether is poured upon the flask which evaporates, causing local cooling and ammonia contracts as a result thereto, producing partial vacuum and hence the red litmus solution rushes in the form of a fountain inside the flask. The solution turns blue. Hence ammonia is soluble in water and the solution is alkaline.

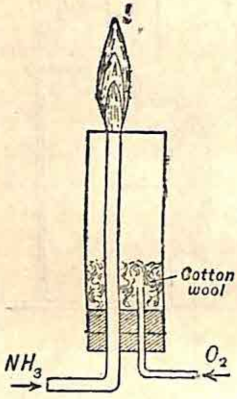


Fig. 49

(iii) It does not support combustion, nor does it burn in air, but in oxygen it burns with a greenish-yellow flame, forming nitrogen and water :

$$4NH_3 + 3O_2 = 6H_2O + 2N_2.$$

Expt.—Dry ammonia is slowly passed through a tube surrounded by a wider tube containing a plug of cotton wool through which diffuses a stream of oxygen (fig. 49)—on ignition, the ammonia readily burns in the oxygen with a greenish yellow flame.

(iv) In presence of platinum gauze as a catalyst, heated to 500°C, a mixture of ammonia with air or oxygen is oxidised to nitric oxide :

$$4NH_3 + 5O_2 = 6H_2O + 4NO.$$

(v) Basic in character, it neutralises acids, yielding ammonium salts : $NH_3+HCl = NH_4Cl$; $2NH_3+H_2SO_4 = (NH_4)_2SO_4$.

Expt.—A piece of paper soaked in concentrated hydrochloric acid is put in a jar of ammonia—dense white fumes of ammonium chloride are formed.

(vi) Ammonia is a mild reducing agent. Ammonia is oxidised to nitrogen and water, when passed over heated lead monoxide or or cupric oxide : $2NH_3+3CuO = 3Cu + N_2 + 3H_2O$.

Chlorine decomposes ammonia liberating nitrogen ; with excess of chlorine the explosive oily liquid nitrogen trichloride is formed :

$$2NH_3+3Cl_2 = N_2+6HCl \; ; \quad 2NH_3+6Cl_2 = 2NCl_3+6HCl.$$

Iodine reacts with a solution of ammonia, yielding the black explosive compound, nitrogen iodide, NI_3, NH_2.

(vii) Ammonia reacts with the alkali metals at red-heat, forming amides, such as sodamide. Water decomposes sodamide, yielding ammonia back :

$$2Na+2NH_3 = 2NaNH_2+H_2. \quad NaNH_2+H_2O = NaOH+NH_3.$$

(viii) When ammonia is dissolved in water, it forms the hydrate ammonium hydroxide which dissociates into ammonia and hydroxyl ions : $NH_3 + H_2O \leftrightharpoons NH_4OH \rightleftharpoons NH_4^+ + OH'$.

The presence of free ammonia in the solution is recognised by its smell. The existence of hydroxyl ions is shown by the alkalinity of the solution and also by its power of precipitating many metallic hydroxides by interaction with the soluble salts of the metals ; e.g.

$$AlCl_3+3NH_4OH = Al(OH)_3+3NH_4Cl\ ;$$
$$FeCl_3+3NH_4OH = Fe(OH)_3+3NH_4Cl.$$

In some cases the precipitated hydroxide redissolves in excess of ammonia solution ; e.g., copper sulphate gives a pale blue precipitate of basic copper sulphate which dissolves in excess of the precipitant forming a deep blue solution :

$$2CuSO_4+2NH_4OH = CuSO_4,Cu(OH)_2+(NH_4)_2SO_4.$$
$$CuSO_4,Cu(OH)_2+(NH_4)_2SO_4+6NH_4OH=2[Cu(NH_3)_4]SO_4+8H_2O.$$

Silver nitrate solution gives a white precipitate which quickly passes into brown oxide, soluble in excess of ammonia.

$$2AgNO_3+2NH_4OH = Ag_2O+2NH_4NO_3+H_2O.$$
$$Ag_2O+4NH_3+H_2O = 2[Ag(NH_3)_2]OH.$$

Liquid ammonia dissolves sodium and potassium to give deep blue solutions.

Tests.—Ammonia is detected by the following properties : (a) its characteristic pungent smell and alkaline reaction, i.e., by the blueing of moist red litmus paper ; (b) it forms dense white fumes of ammonium chloride with gaseous hydrochloric acid ; (e) it produces a yellow or brown colouration or a precipitate with *Nessler's reagent* (an alkaline solution of potassium mercuric iodide, K_2HgI_4). This is the most delicate test for ammonia and ammonium salts ; (d) it blackens a piece of paper soaked in mercurous nitrate solution.

Uses.—(i) Huge quantities of ammonia are used in the manufacture of *fertilizers*, such as *ammonium sulphate*, and ammonium phosphate ; *nitric acid* by the Ostwald process, *sodium carbonate* by the Solvay process, and urea, $CO(NH_2)_2$.

(ii) Liquid ammonia is used as a refrigerant in ice-making.

(iii) Ammonia is transported in cylinders and then 'cracked' (i.e., decomposed into its elements by heat) to supply hydrogen for the purposes of welding and cutting of metals.

(iv) Ammonia and ammonium salts are used in medicine—'smelling salt' contains solid ammonium carbonate and a little lime water.

(v) Ammonia is used as cleansing agent for removing grease and as a reagent in laboratories.

Ammonia by other methods.—(i) By the reduction of the oxides of nitrogen ; e.g., by passing a mixture of nitric oxide and hydrogen over heated spongy platinum :

$$2NO + 5H_2 = 2NH_3 + 2H_2O.$$

(ii) By heating a solution of a nitrate or nitrite with zinc and strong caustic soda solution : $NaNO_3 + 8H = NaOH + NH_3 + 2H_2O$.

(iii) By heating a metallic nitride with an alkali :

$$Mg_3N_2 + 6HOH = 3Mg(OH)_2 + 2NH_3$$
$$AlN + NaOH + H_2O = NaAlO_2 + NH_3.$$

These methods are not suitable for the laboratory preparation of ammonia.

Manufacture of ammonia.—(i) **Gasworks ammonia.**—Ammonia is obtained as a by-product in the manufacture of coal-gas. Coal contains about 1—1.5 per cent nitrogen and also some hydrogen. When coal is subjected to destructive distillation for the manufacture of coal-gas, the nitrogen is converted mainly into ammonia which collects in the *ammoniacal liquor* as an aqueous solution—the liquor containing both free ammonia and ammonium salts. The liquor is heated with steam to drive out the free ammonia, and the residue is then treated with milk of lime and additional steam to liberate the ammonia from its salts. The ammonia is absorbed in 60 per cent sulphuric acid, yielding crystals of ammonium sulphate, mostly used in agriculture as a fertiliser.

$$2NH_3 + H_2SO_4 = (NH_4)_2SO_4.$$

The yield is about 20-25 lbs. of ammonium sulphate per ton of coal.

(ii) Synthetic ammonia : Haber's process.—Synthesis of ammonia from its elements is utilised in the Haber's process :

$$N_2+3H_2 \leftrightharpoons 2NH_3+2\times 11{,}000 \text{ calories.}$$

The reaction is *exothermic* (i.e., attended with evolution of heat) and reversible. The yield of ammonia diminishes with rise of temperature. The reaction should, therefore, be conducted at a low temperature. But at a low temperature the speed of the reaction is slow, and hence the reaction is carried out at an *optimum temperature* at which the speed of the reaction is not too slow, nor the yield of ammonia too low. *The optimum temperature is about* 550°C *in the Haber's process.*

The speed of the reaction is increased by using a catalyst—*finely divided iron* with 'promoters' such as traces of molybdenum, or a mixture of aluminium oxide and potassium oxide, is the catalyst used.

The formation of ammonia takes places with a contraction in volume and hence it is favoured at high pressures. A pressure of 200 *atmospheres* is employed in the Haber's process.

The table shows how the yield of ammonia depends on temperature and pressure—equilibrium percentages by volume of ammonia are as follows :

Temperature	10	100	2000	1000 atm. pressure.
400°C	3.85	25	36.3	80
500°	2.1	10.6	17.6	57.5
550°	0.76	6.8	12.0	41
600°	0.5	4.5	8.3	31.5

A mixture of pure and dry nitrogen and hydrogen in the ratio of 1 : 3 by volume is compressed to 200 atmospheres and sent by

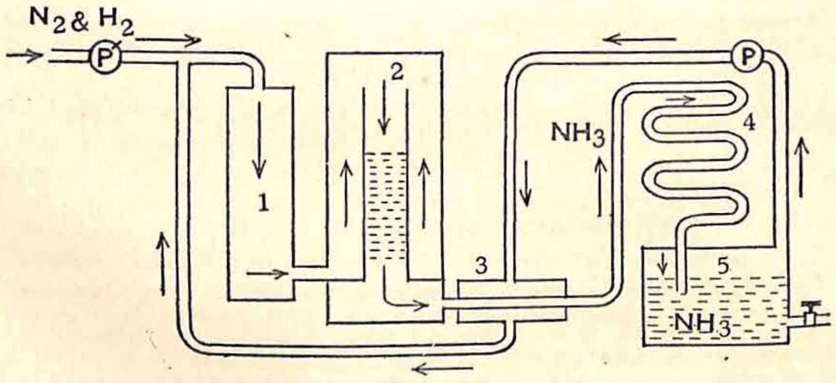


Fig. 50

means of a pump P′ via a sodalime drying chamber (1) into the catalyst chamber (fig. 50) which is a tube (2) of chrome-vanadium steel The gases first circulate around the outside of the central tube (2) and thereby get preheated and then pass down the tube containing trays of promoted catalyst kept at 550° by being heated electrically ; but once the reaction starts external heating is unnecessary. Nitrogen and hydrogen react to yield ammonia. The reaction is exothermic, and hence the incoming mixture of nitrogen and hydrogen is circulated round the catalyst-tube for maintaining the optimum temperature.

The gases leaving the catalyst chamber contain about 12% ammonia and the rest unconverted nitrogen and hydrogen, and pass through a heat-interchanger (3) to preheat the entering gases. The ammonia formed is removed by absorption in water, and for this the cooled gas is brought in contact with water in washers (5) *while still under high pressure*, producing a 25% solution of ammonia. The unreacted nitrogen and hydrogen are circulated by a pump P via the heat-interchanger (3) and are dried in the soda-lime tower, and these together with more nitrogen and hydrogen, are recirculated by a pump P′ to the catalyst chamber and so the process continues.

The unreacted nitrogen and hydrogen, instead of being recirculated, are blown off from time to time to remove the argon which unavoidably enters the plant with the nitrogen.

A pressure of 900 atmospheres is used in Claude's process—in high pressure processes ammonia is removed by cooling and liquefaction under pressure.

The required mixture of nitrogen and hydrogen is usually made from :

(a) the nitrogen obtained from liquid air by fractionation and the hydrogen prepared electrolytically.

(b) a mixture of water gas ($CO + H_2$) and producer gas ($CO + N_2$)—these gases in correct proportion are mixed with excess steam and passed over a heated catalyst (mixture of $Fe_2O_3 + Cr_2O_3$) at 450°C, when CO is oxidised to CO_2, thus $CO + H_2O \leftrightharpoons CO_2 + H_2$. The CO_2 is removed by absorption with water under pressure and last traces of CO by washing with ammoniacal cuprous formate solution under 200 atmospheres—the pure nitrogen-hydrogen mixture is ready for the process ; the method was used in original Haber plant.

There is a Haber plant is Mysore State. The Sindri Fertiliser project hase gone into operation to produce ammonia by the Haber process, getting the nitrogen-hydrogen mixture from *air, coal and steam.*

The ammonia may be absorbed in a suspension of crushed calcium sulphate (calcined gypsum) in water and carbon dioxide passed into the liquid—the precipitated calcium carbonate is filtered off and ammonium sulphate is crystallised out from the filtrate ; a process extensively utilised commercially. Ammonia is thus converted into ammonium sulphate without using sulphuric acid.

$$2NH_3 + CO_2 + H_2O + CaSO_4 = (NH_4)_2SO_4 + CaCO_3.$$

Ammonium sulphate is produced by this method in the Sndri fertiliser plant.

Oxides and oxyacids of nitrogen

The chief oxides and oxyacids of nitrogen are the following :

Nitrous oxide, N_2O
Nitric oxide, NO

Hyponitrous acid, $H_2N_2O_2$

Nitrogen trioxide, N_2O_3	Nitrous acid, HNO_2
Nitrogen tetroxide, N_2O_4, or nitrogen dioxide, NO_2	$N_2O_4 \leftrightharpoons 2NO_2$
Nitrogen pentoxide, N_2O_5	Nitric acid, HNO_3

All the oxides of nitrogen are endothermic at room temperature.

Nitric acid HNO_3

Density at 15°, 1.52. Boiling point 78.2°. Freezing point −41.3°.

Free nitric acid, produced by lightning flashes, occur in traces in air. It is found in the form of nitre (potassium nitrate) in the soil of tropical countries like India, and as sodium nitrate (Chile salt petre) in Chile in South America.

Laboratory preparation.—Nitric acid is volatile—a less volatile acid like sulphuric acid displaces it from a nitrate. Hydrochloric acid though stronger than sulphuric acid is not used in the preparation of nitric acid, since hydrochloric acid is volatile.

In the laboratory nitric acid is prepared by distilling a mixture of potassium or sodium nitrate with concentrated sulphuric acid, when the following reaction takes place, forming potassium (or sodium) hydrogen sulphate and evolving nitric acid vapours.

$$KNO_3+H_2SO_4 = KHSO_4+HNO_3\ ;$$
$$NaNO_3+H_2SO_4 = NaHSO_4+HNO_3.$$

Equal parts by weight of potassium nitrate and concentrated sulphuric acid are taken in a stoppered glass retort (fig. 16) the stem of which communicates with a water-cooled receiver. Nitric acid distils on moderate heating at about 200°C and collects in the receiver.

With excess of nitre and at a higher temperature of about 800°C a further reaction occurs ; the potassium (or sodium) hydrogen sulphate being converted into normal sulphate :

$$KNO_3+KHSO_4 = K_2SO_4+HNO_3.$$

But the reaction is not carried to this stage, as

(i) the glass retort would crack at the high temperature required ;

(ii) the normal sulphate forms a solid mass in the retort which it is difficult to remove ; and

(iii) most of the acid would decompose at the high temperature :

$$4HNO_3 = 2H_2O+4NO_2+O_2.$$

The acid contains water and oxides of nitrogen formed by the decomposition of the acid as impurities, and is brown in colour. It may be concentrated up to 98% by distillation with concentrated sulphuric acid : oxides of nitrogen are removed by bubbling air through the acid till colourless. Pure nitric acid may be obtained as colourless crystals by freezing the 98 per cent acid at −42°C.

Properties.—(i) A colourless, fuming liquid with a choking smell, the acid is soluble in water in all proportions.

(ii) It is a *strong monobasic acid*—the acid is readily ionised in solution and is, therefore, a strong acid :

$$HNO_3 \leftrightharpoons H^+ + NO_3'$$

It turns blue litmus red and reacts with alkalis, yielding salt and water : $HNO_3+NaOH = NaNO_3+H_2O$.

(iii) It is a *highly corrosive liquid* and produces painful blisters if it comes in contact with skin which it attacks, causing a yellow stain. Other organic bodies like leather, silk, etc., are also stained yellow by strong nitric acid.

Cotton which is almost pure cellulose, is converted into *nitro-cellulose* by the action of concentrated HNO_3 in presence of concentrated H_2SO_4—the nitro-cellulose is employed under the name of *gun-cotton* in explosives. Glycerine under similar conditions, produces *nitro-glycerine*, also called *Nobel's oil*, which is absorbed in kieselguhr for making *dynamite*.

Oil of turpentine bursts into flame with evolution of black clouds of carbon, when added to concentrated nitric acid in a basin.

(iv) It readily decomposes on heating, yielding water, brown vapours of nitrogen dioxide and oxygen.

$$4HNO_3 = 2H_2O+4NO_2+O_2.$$

(v) It is a *powerful oxidising agent.*—Ready liberation of oxygen from nitric acid makes it a powerful oxidising agent, particularly when hot and concentrated. (a) Hot concentrated acid oxidises sulphur to sulphuric acid, iodine to iodic acid, and phosphorus to phosphoric acid. $S+2HNO_3 = H_2SO_4+2NO$;

$$3I_2+10HNO_3 = 6HIO_3+10NO+2H_2O.$$

$$4P+10HNO_3+H_2O = 4H_3PO_4+5NO+5NO_2.$$

(b) Glowing charcoal burns brilliantly in strong acid ; warmed saw-dust bursts into flame in the acid :

$$C+4HNO_3 = CO_2+4NO_2+2H_2O.$$

Some saw-dust is heated on a sand bath in a basin until it begins to char; it inflames on pouring on it a few drops of *fuming nitric acid* very carefully from a test tube. Yellow-coloured **fuming nitric acid** containing dissolved oxides of nitrogen, is a powerful oxidising agent, and is made by distilling concentrated nitric acid with a little starch, which reduces some nitric acid to the nitrogen oxides NO and NO_2.

(c) Concentrated nitric acid oxidises ferrous salts to ferric salts—the reaction is quantitative. Thus the acid converts ferrous sulphate in presence of sulphuric acid to ferric sulphate :

$$6FeSO_4+3H_2SO_4+2HNO_3 = 3Fe_2(SO_4)_3+2NO+4H_2O.$$

(d) Hot dilute or cold concentrated nitric acid liberates sulphur from hydrogen sulphide and iodine from potassium iodide :

$$3H_2S+2HNO_3 = 3S+2NO+4H_2O.$$

$$6KI+8HNO_3 = 3I_2+6KNO_3+2NO+4H_2O.$$

Sulphur dioxide is oxidised to sulphuric acid by nitric acid :

$$2HNO_3+SO_2 = H_2SO_4+2NO_2.$$

(e) Hot concentrated nitric acid reacts with concentrated hydrochloric acid, yielding chlorine, nitrosyl chloride and water :

$$3HCl+HNO_3 = Cl_2+NOCl+2H_2O.$$

A mixture of concentrated nitric acid (1 vol.) and hydrochloric acid (3 vols.) is known as **aqua regia :** it dissolves gold and platinum. $Au+4HCl+HNO_3 = HAuCl_4+NO+2H_2O$.

(vi) **Reactions with metals.**—Nitric acid reacts with all metals except gold, platinum, tantalum, rhodium and iridium : iron and chromium become *'passive'* in the concentrated acid : *aluminium is scarcely attacked by cold nitric acid.* Tin and antimony are converted into their oxides. The remaining metals yield nitrates. Since in its action upon metals, nitric acid acts both as *an acid* and *an oxidising agent*, the attack on the metal is always (except in the case of very dilute acid and magnesium or manganese) accompanied by reduction of the nitric acid to oxides of nitrogen, nitrogen, or ammonia, etc.—the nature of the product depending upon (a) *strength of the acid*, (b) *temperature*, (c) *nature of the metal*, and (d) *products of reaction in the solution.* Hydrogen is evolved only by magnesium or manganese, acting upon very dilute (1 or 2 per cent) and cold nitric acid :

$$Mg+2HNO_3 = Mg(NO_3)_2+H_2.$$

The mechanism of reduction of nitric acid by metals may be explained by assuming that the initial attack of metals on nitric acid liberates nascent hydrogen which then reduces the excess of nitric acid. The theory explains the action of such metals as iron and zinc which are more electro-positive than hydrogen. The action of zinc upon strong nitric acid, yielding nitrogen dioxide may be explained as follows :

$$\begin{aligned} Zn + 2HNO_3 &= Zn(NO_3)_2 + 2H \\ 2HNO_3 &= H_2O + 2NO_2 + O \\ 2H + O &= H_2O \\ \hline Zn + 4HNO_3 &= Zn(NO_3)_2 + 2H_2O + 2NO_2 \end{aligned}$$

But the metals such as copper, silver and mercury are less electro-positive than hydrogen. It is, therefore, suggested that the initial step in the attack is the oxidation of the metal to its oxide which then dissolves in the acid.

$$\begin{aligned} 3Cu + 2HNO_3 &= H_2O + 2NO + 3CuO. \\ 3CuO + 6HNO_3 &= 3H_2O + 3Cu(NO_3)_2. \\ \hline 3Cu + 8HNO_3 &= 3Cu(NO_3)_2 + 2NO + 4H_2O. \end{aligned}$$

Action of nitric acid upon few metals—Different oxides of nitrogen or ammonium nitrate are formed, depending mainly on the strength of acid :

Copper :

(i) Hot concentrated $Cu + 4HNO_3 = Cu(NO_3)_2 + 2H_2O + 2NO_2$.
(i) Cold dilute (1: 1) $3Cu + 8HNO_3 = 3Cu(NO_3)_2 + 4H_2O + 2NO$
(iii) Cold dilute $4Cu + 10HNO_3 = 4Cu(NO_3)_2 + 5H_2O + N_2O$

Zinc :

(i) Hot concentrated $Zn + 4HNO_3 = Zn(NO_3)_2 + 2H_2O + 2NO_2$
(ii) Cold dilute $3Zn + 8HNO_3 = 3Zn(NO_3)_2 + 4H_2O + 2NO$
(iii) Cold very dilute $4Zn+10HNO_3 = 4Zn(NO_3)_2+3H_2O+NH_4NO_3$.
$4Zn+10HNO_3 = 4Zn(NO_3)_2 + 5H_2O +N_2O$.

Zinc dissolves in dilute nitric acid to form ammonium nitrate—some nitrous oxide and nitric oxide are also evolved.

Iron :

(i) Fairly concentrated or hot dilute $Fe + 4HNO_3 = Fe(NO_3)_3 + 2H_2O + NO$
(ii) Cold dilute $4Fe + 10HNO_3 = 4Fe(NO_3)_2 + 3H_2O + NH_4NO_3$
(iii) Concentrated or fuming acid does not dissolve iron but renders it *passive*.

Mercury :

(i) Hot concentrated $Hg + 4HNO_3 = Hg(NO_3)_2 + 2H_2O + 2NO_2$

(ii) Cold dilute $6Hg + 8HNO_3 = 3Hg_2(NO_3)_2 + 4H_2O + 2NO$

Tin :

(i) Cold dilute $4Sn + 10HNO_3 = 4Sn(NO_3)_2 + 3H_2O + NH_4NO_3$.

(ii) Hot concentrated acid produces stannic nitrate, which is readily hydrolysed to a white precipitate of metastannic acid, $H_2Sn_5O_{11}$, $4H_2O$, the latter decomposing by heat into tin dioxide and water.

$$5Sn + 20HNO_3 = H_2Sn_5O_{11}.4H_2O + 5H_2O + 20NO_2.$$

Silver : (i) Hot dilute $Ag + 2HNO_3 = AgNO_3 + H_2O + NO$.

Tests for Nitric Acid and Nitrates.—(i) Reddish brown fumes of nitrogen dioxide are evolved when nitric acid or a nitrate is warmed with concentrated sulphuric acid and copper turnings. Copper dissolves in nitric acid, giving a bluish-green solution.

(ii) Rose-red colour is produced on adding a nitrate or nitric acid to a solution of brucine in concentrated sulphuric acid.

(iii) **The brown ring test** for nitrate and nitric acid.—An excess of freshly prepared solution of ferrous sulphate is added to a cold dilute solution of a nitrate in a test tube, and concentrated sulphuric acid is carefully poured into the liquid so as to form a heavy bottom layer ; a brown ring is formed at the junction of the two liquids. *Nitrites interfere with the ring test.*

The ferrous sulphate reduces the nitric acid to nitric oxide NO, which reacts with excess of ferrous sulphate, yielding the brown nitroso compound $(Fe.NO)SO_4$, which appears as a brown ring at the junction of the liquids. The nitroso compound is unstable and decomposes on warming into nitric oxide and the ferrous salt, and consequently while performing the ring test, the test tube is cooled under the tap during the addition of sulphuric acid.

$$2HNO_3 + 3H_2SO_4 + 6FeSO_4 = 3Fe_2(SO_4)_3 + 2NO + 4H_2O$$

$$FeSO_4 + NO \leftrightharpoons (Fe.NO)SO_4$$

A nitrate is converted to ammonia by heating with zinc and strong caustic soda solution.

$$NaNO_3 + 4Zn + 7NaOH = NH_3 + 4Na_2ZnO_2 + 2H_2O.$$

Uses of Nitric Acid.—Besides its uses in the laboratory nitric acid finds applications : (i) in the production of explosives such as dynamite, gun cotton, nitro-glycerine, picric acid, trinitrotoluene (T.N.T.), and ammonium nitrate. Nitre is a constituent of gunpowder.

(ii) in the manufacture of sulphuric acid, coal tar colours, nitrates and fertilisers.

(iii) in etching designs on wares of brass and bronze, and staining silk, wool, etc., yellow ; in the 'pickling' of metals before electro-plating ; in the separation of gold and silver.

(iv) in the manufacture of celluloid, collodion, cellophane, rayon, lacquers and other nitrocellulose products.

Manufacture of nitric acid.—(i) *Distillation of sodium nitrate with concentrated sulphuric acid.*—Chile salt petre and cencentrated sulphuric acid (in 3 : 2 molecular proportions) are placed in a large cast-iron retort which is connected by water-cooled earthenware or silica pipes to a series of stoneware bottles, and then with a tower, filled with stoneware balls, down which water is sprayed (fig. 51). The retort is set in a brick work furnace, and is carefully heated by coke fires to about 200-250°C. The vapours of nitric acid which is evolved according to the equation,

$$3NaNO_3+2H_2SO_4 = Na_2SO_4+NaHSO_4+3HNO_3$$

are cooled by passing through the silica spirals cooled in water and are condensed in the stone-ware bottles as concentrated nitric acid.

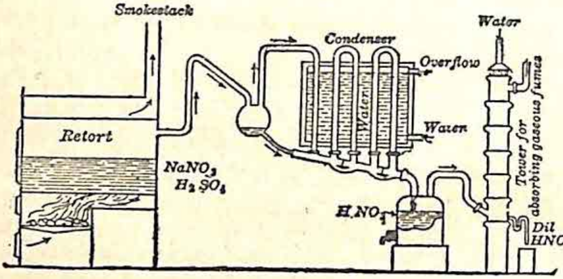


Fig. 51

Any uncondensed vapour which is largely nitrogen dioxide (from the decomposition of nitric acid), is absorbed by water in the tower yielding weak nitric acid :

$$4NO_2+O_2+2H_2O = 4HNO_3.$$

The residue in the retort which is a mixture of sodium sulphate and bisulphate is tapped out in the liquid state through an exit at the bottom of the retort. When solid, it is known as **nitre-cake.** The acid is of 90—95 per cent strength. It may be concentrated to 98 per cent by distillation with strong sulphuric acid.

Nitric acid *vapour* does not corrode iron, which is attacked by the liquid acid. The method—though easy to carry out and largely used in India, is based on *imported* Chile salt petre.

(ii) **The catalytic oxidation of ammonia : Ostwald process.**—In this process ammonia is oxidised to nitric oxide by the oxygen of air in presence of heated *platinum gauze catalyst*—more than 90% of NH_3 is converted into NO :

$$4NH_3+5O_2 = 4NO+6H_2O+305{,}000 \text{ calories.}$$

An excess of air over that required theoretically to form nitric oxide is necessary. The air is preheated to about 500°C in a heat exchanger (2), by the hot gases produced by the oxidation of ammonia, and then freed from dust particles by filtration through woollen cloth in the air filter (3). A mixture of pure and dry ammonia (usually the synthetic ammonia from the Haber plant) and the preheated air in the proportion of 1 : 7.5 by volume is *rapidly* (time of contact with catalyst is about 1/1000 second ; otherwise ammonia is oxidised to nitrogen) passed through a layer of fine-mesh *platinum gauze catalyst* stretched across an aluminium box (1) (fig. 52) called a converter—the catalyst is initially brought to the reaction temperature of 750°—900°C by electrical heating ; once started the *exothermic reaction* proceeds automatically. The hot products of the reaction in passing through the heat-interchanger heats the incoming air and so the process continues without external heating.

The somewhat cooled products of the reaction which contain nitric oxide, some nitrogen, excess air and steam, after leaving the heat-interchanger (2), are cooled to about 50°C in an aluminium pipe (4) where the nitric oxide is oxidised to nitrogen dioxide by the oxygen of the accompanying excess air. $2NO+O_2 = 2NO_2$. The nitrogen dioxide is then absorbed in water in several stainless steel towers (5) packed with broken quartz to form nitric acid.
$2NO_2+H_2O=HNO_3+HNO_2$; $3HNO_2=HNO_3+2NO+H_2O$.

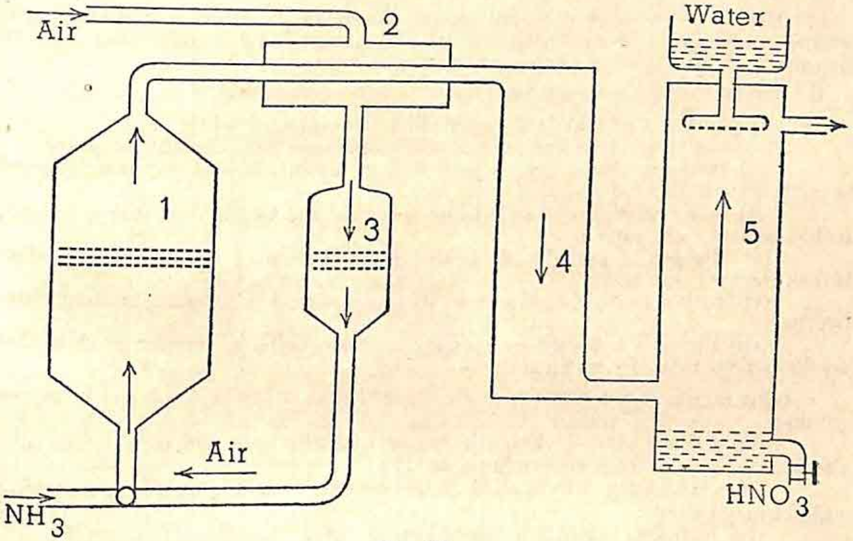


Fig. 52

The nitric oxide liberated is reoxidised by the air present, forming NO_2 which re-enters the reaction. $2NO+O_2=2NO_2$. A 50% solution of nitric acid is collected from the bottom of the tower.

The dilute acid may be concentrated by distillation until the liquid attains the composition of constant boiling point containing 68% HNO_3 (boiling point 121°) ; this is the ordinary commercial acid of density 1.414. It may be concentrated to 98% by distillation with concentrated sulphuric acid.

Ezercise

1. How may nitrogen be obtained from (*a*) air, (*b*) ammonia, (*c*) nitric acid, (*d*) ammonium nitrite ? Under what conditions does nitrogen combine with, (*i*) hydrogen, (*ii*) oxygen, (*iii*) magnesium and (*iv*) calcium carbide ? Describe the action of water on the products formed in each case.

2. What are the chief constituents of air ? Describe Lavoisier's experiment on the composition of air. Show that air is a mechanical mixture.

3. How would you obtain a specimen of dry ammonia gas ? State its chief properties, tests and uses. How and under what conditions does it react with (*i*) lead oxide, (*ii*) chlorine, (*iii*) sodium, (*iv*) carbon dioxide, (*v*) ferric chloride solution, and (*vi*) copper oxide ?

4. Give an outline of Haber's method of manufacturing ammonia from atmospheric nitrogen. Describe its reaction with : (*i*) copper sulphate, (*ii*) silver chloride, (*iii*) mercurous chloride, (*iv*) calcium sulphate and carbon dioxide ?
P.U. (Cal.), 1961

5. How is nitric acid prepared in the laboratory ? How may the nitrogen present in nitric acid be converted into (*i*) ammonia, (*ii*) nitric oxide, and (*iv*) free nitrogen ? State its chief properties, uses and tests.

6. Explain what happens when :

(i) glowing charcoal is dropped into concentrated nitric acid ;

(ii) a mixture of air and ammonia is passed over heated platinum gauze ;

(iii) strong sulphuric acid is poured carefully into ferrous sulphate dissolved in cold dilute nitric acid ;

(iv) ammonia is passed over heated sodium, and the product that is formed, is then treated with water ;

(v) nitrogen is passed over heated aluminium, and the resulting product is then warmed with water ;

(vi) carbon dioxide is led into a suspension of calcium sulphate in ammonium hydroxide ;

(vii) nitrogen is passed over heated calcium carbide, and the product that results is then treated with steam ;

(viii) ammonium hydrate is gradually added in excess to a solution of copper sulphate.

(ix) sodium nitrate solution is heated with zinc dust and caustic soda, and the evolved gas is led into sulphuric acid.

(x) a gas obtained by heating ammonium nitrite is led into a tube containing red-hot magnesium ;

(ix) hydrogen sulphide is passed into strong nitric acid.

7. Give an outline of Ostwald's method of making nitric acid from ammonia. Describe an experiment to show that nitric acid is an oxidising agent.

XIV

THE HALOGENS

The elements fluorine, chlorine, bromine and iodine are called *halogens*, or 'salt-forming' elements (*hals* means sea-salt), as the last three are contained in sea-water, and their sodium salts resemble the sea-salt, sodium chloride. Moissan isolated fluorine in the year 1886.

Chlorine

Formula Cl_2. Valency 1. B. pt.—34.6°. M. pt.—101.6°. Atomic weight 35.457. Atomic number 17. Solubility, 1 vol. of water dissolves 4.6 volumes at 0°. Liquefaction, liquefies at 6 atmospheres at 15°.

Chlorine does not occur free in nature but is found in large quantities as *common salt* or *rock salt*, NaCl. Besides, it occurs in the Stassfurt deposits in Germany as *sylvine*, KCl, and *carnallite*, KCl, $MgCl_2$, $6H_2O$. It also occurs as *hornsilver*, AgCl.

Laboratory preparation.—Chlorine is usually prepared in the laboratory by the oxidation of hydrochloric acid with (a) *pyrolusite* (mineral form of manganese dioxide, MnO_2), or (b) *potassium permanganate*, $KMnO_4$.

(a) Powdered manganese dioxide (pyrolusite) is taken in a flask fitted with a thistle funnel and a delivery tube (fig. 53). Strong hydrochloric acid is poured down the funnel in quantity ; chlorine is liberated as a greenish yellow gas on gently warming the flask. The gas is bubbled through water in a wash-bottle to dissolve out hydrochloric acid vapours and then through concentrated sulphuric acid to remove moisture. The pure and dry gas is then collected in dry gas jars by the upward displacement of air (it is 2½ times heavier than air). It may also be collected over saturated brine or hot water in which it is much less soluble, but not over water in which it dissolves rather readily, *nor over mercury which it attacks* :

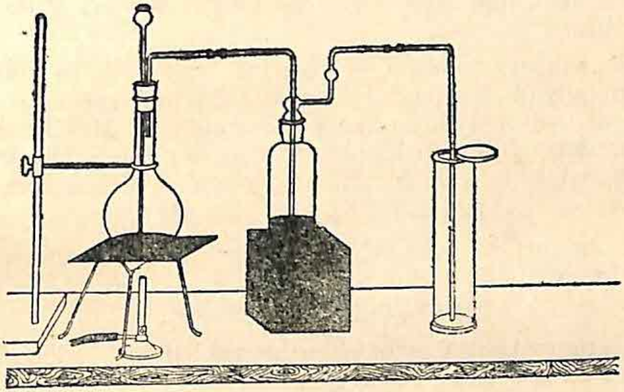


Fig. 53

$$MnO_2+4HCl = MnCl_2+2H_2O+Cl_2.$$

The action of manganese dioxide upon hydrochloric acid take place in two steps ; the dark brown solution formed in the cold contains manganese trichloride which decompose on warming with liberation of chlorine :

$$2MnO_2 + 8HCl = 2MnCl_3 + Cl_2 + 4H_2O = 2MnCl_2 + 2Cl_2 + 4H_2O.$$

Instead of hydrochloric acid and manganese dioxide a mixture of *common salt,* 50 per cent *sulphuric acid* and *manganese dioxide* may be heated to prepare chlorine.

$$2NaCl+2H_2SO_4 = 2NaHSO_4+2HCl.$$
$$MnO_2+H_2SO_4 = MnSO_4+H_2O+O.$$
$$2HCl+O=H_2O+Cl_2$$

$$MnO_2+2NaCl+3H_2SO_4 = MnSO_4+2NaHSO_4+Cl_2+2H_2O.$$

(b) A convenient supply of chlorine may be obtained by dropping cold concentrated hydrochloric acid upon crystals of potassium permanganate taken in a conical flask. The gas is washed and dried as in method (a). The reaction is :

$$2KMnO_4 + 16HCl = 2KCl + 2MnCl_2 + 8H_2O + 5Cl_2.$$

Chlorine is also obtained : (i) By the action of dilute acid on bleaching powder.

$$Ca(OCl)Cl + 2HCl = CaCl_2 + H_2O + Cl_2.$$

(ii) By heating a mixture of potassium dichromate and concentrated hydrochloric acid :

$$K_2Cr_2O_7 + 14HCl = 2KCl + 2CrCl_3 + 3Cl_2 + 7H_2O.$$

Properties.—(i) Chlorine is a heavy (about 2½ times as heavy as air) *greenish yellow*, highly poisonous gas with irritating smell and corrosive properties ; it is easily liquefied by cooling and compression.

(ii) It is fairly soluble in water but is very much less soluble than hydrochloric acid, and *hence may be separated from traces of the latter by washing with water*

(a) The aqueous solution of chlorine, yellowish in colour and smelling strongly of chlorine is known as **chlorine water ;** it contains a mixture of hydrochloric and hypochlorous acid HOCl, the latter liberates nascent oxygen on keeping and particularly *in bright sunlight.* Hence the oxidising and bleaching properties of chlorine water :

$$Cl_2+H_2O = HCl+HOCl = 2HCl+O.$$

(b) In bright sunlight chlorine directly decomposes water, liberating oxygen ; the reaction is reversible :

$$2H_2O+2Cl_2 \leftrightharpoons 4HCl+O_2.$$

(c) A saturated solution of chlorine, cooled to 0°, deposits white crystals of *chlorine hydrate*, $Cl_2,6H_2O$.

(iii) It does not burn but *supports combustion* of many elements such as phosphorus, arsenic, antimony, bismuth, sodium and copper.

(a) Finely powdered arsenic or antimony, when sprinkled into a jar of chlorine, spontaneously catches fire, yielding a shower of sparks. Pieces of white phosphorus or thin copper foils, on being similarly introduced, ignite spontaneously in the gas.

(b) When chlorine is passed over sodium heated in a bulb tube, the metal burns with a bright yellow flame.

$$2As + 3Cl_2 = 2AsCl_3 \qquad 2Na + Cl_2 = 2NaCl$$
$$Cu + Cl_2 = CuCl_2. \qquad 2Sb + 5Cl_2 = 2SbCl_5$$
$$2P + 5Cl_2 = 2PCl_5 \qquad 2P + 3Cl_2 = 2PCl_3$$

Chlorine directly unites with most metals and many non-metals, yielding chlorides ; but **it is without action upon carbon, nitrogen and oxygen**—their chlorides being prepared indirectly.

(iv) It has great affinity for hydrgoen. When exposed to *sunlight* a mixture of hydrogen and chlorine explodes violently to form hydrogen chloride : $H_2+Cl_2 = 2HCl$.

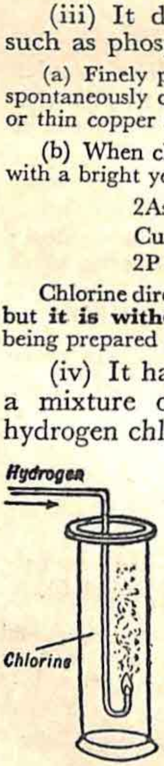


Fig. 54

(a) A burning jet of hydrogen continues burning with a greenish flame, when introduced in a jar of chlorine, forming hydrogen chloride (fig. 54). In presence of activated charcoal hydrogen and chlorine readily combine to yield hydrochloric acid—a process of commercial importane.

(a) A lighted candle, on being inserted into a jar of chlorine, burns with a small dull-red flame with copious deposition of soot and forming hydrochloric acid.

(c) A piece of paper soaked in turpentine which is a hydrocarbon of the formula $C_{10}H_{16}$, bursts into flame when plunged into chlorine, yielding a cloud of soot mixed with fumes of HCl :

$$C_{10}H_{16} + 8Cl_2 = 10C + 16HCl.$$

In the experiments (b) and (c) chlorine attacks the hydrocarbons (candle is made up of paraffin wax which is a mixture of hydrocarbons), uniting with the hydrogen to form hydrochloric acid and not with carbon which, therefore, deposits as soot.

(v) **Action of chlorine on alkalis.**—(a) Chlorine reacts with a *cold alkali* e.g., NaOH, KOH or $Ca(OH)_2$, solution, to give the chloride and **hypochlorite** of the metal *as long as the solution is alkaline*.

$$\begin{array}{c} Cl_2+H_2O = HCl+HOCl. \\ HCl+HOCl+2NaOH = NaCl+NaOCl+2H_2O. \\ \hline Cl_2+2NaOH = NaCl+NaOCl+H_2O. \end{array}$$

But when all the alkali is removed, i.e., *in presnece of excess of chlorine*, the hypochlorite is readily converted into *chlorate*.

Chlorine dissolves in alkaline solution of hydrogen peroxide, giving off oxygen.

$$H_2O_2 + 2NaOH + Cl_2 = 2NaCl + 2H_2O + O_2.$$

(b) *Hot solution of the alkali* also yields chloride and **chlorate** of the metal through the intermediate formation of hypochlorite :

$$\begin{array}{c} 3Cl_2+6NaOH = 3NaCl+3NaOCl+3H_2O. \\ 3NaOCl = 2NaCl+NaClO_3. \\ \hline 3Cl_2+6NaOH = 5NaCl+NaClO_3+3H_2O. \end{array}$$

(c) A solution of calcium hydroxide or milk of lime reacts similary. $2Ca(OH)_2(\text{cold})+2Cl_2 = CaCl_2+Ca(OCl)_2+2H_2O.$

$$6Ca(OH)_2(\text{hot})+6Cl_2 = 5CaCl_2+Ca(ClO_3)_2+6H_2O.$$

Chlorine reacts with dry slaked lime forming bleaching powder :

$$Ca(OH)_2 + Cl_2 = Ca(OCl)Cl + H_2O.$$

Chlorine reacts with calcium oxide at a red heat, yielding calcium chloride and oxygen : $2CaO + 2Cl_2 = CaCl_2 + O_2$.

(vi) **Oxidising action of chlorine.**—It oxidises stannous salts to stannic salts, and ferrous salts to ferric salts :

$$SnCl_2+Cl_2 = SnCl_4\ ;\quad 2FeCl_2+Cl_2 = 2FeCl_3.$$

Chlorine reacts with ammonia, liberating nitrogen, but nitrogen trichloride is formed if chlorine is in excess.

$$3Cl_2+8NH_3 = 6NH_4Cl+N_2\ ;\qquad 3Cl_2+NH_3 = NCl_3+3HCl.$$

In presence of water, chlorine can also oxidise by the addition of oxygen to a compound. Thus it converts sulphurous acid to sulphuric acid :

$$H_2SO_3 + H_2O + Cl_2 = H_2SO_4 + 2HCl.$$

Chlorine displaces sulphur from hydrogen sulphide and iodine from hydrogen iodide :

$$H_2S+Cl_2 = 2HCl+S\ ;\quad 2HI+Cl_2 = 2HCl+I_2.$$

It can also displace bromine from a bromide and iodine from an iodide : $2KI+Cl_2 = 2KCl+I_2$; $2KBr+Cl_2 = 2KCl+Br_2$.

Expt.—Chlorine water is added to potassium iodide solution and then shaken with a little carbon disulphide—carbon disulphide dissolves the liberated iodine, forming a *violet layer*. The experiment is repeated with potassium bromide solution ; the liberated bromine colours the carbon disulphide layer *reddish brown*.

(vii) **Bleaching action of chlorine.**—*Chlorine bleaches vegetable colours in presence of moisture—dry chlorine does not bleach.* Moist chlorine liberates nascent oxygen : $H_2O+Cl_2 = 2HCl+O.$

The nascent oxygen oxidises the vegetable colouring matter and the colour is bleached, i.e., *chlorine bleaches by oxidation.*

Expt.—A green leaf, a piece of red cloth, a piece of printed paper brushed with writing ink,—all are placed, one in each, in a set of jars containing *moist* chlorine. All the articles are found to be bleached *except the prints. The printer's ink contain free carbon which is not acted on by chlorine.*

The experiment is repeated with dry chlorine but with a negative result.

(viii) Chlorine forms *additive compounds* with many unsaturated substances, e.g., $CO + Cl_2 = COCl_2$ (carbonyl chloride) :

$C_2H_4 + Cl_2 = C_2H_4Cl_2$ (ethylene dichloride).

Tests.—(i) Chlorine is detected by its greenish yellow colour, irritating smell and bleaching properties.

(ii) Chlorine liberates iodine from potassium iodide, which turns starch blue.

Uses.—(i) As a bleaching agent in paper and textile industries.

(ii) As a disinfectant in the sterilisation of water, and in dressing wounds—Carrel-Dakin solution used for the purpose is obtained by the action of chlorine upon washing soda.

(iii) As a poison gas, and for making poison gases, such as phosgene, mustard gas and chloropicrin.

(iv) For the manufacture of bleaching powder, hydrochloric acid, bromine, hypochlorite, and many chlorides such as $AlCl_3$, $MgCl_2$, $SnCl_4$, and PCl_3.

Bromine

Formula Br_2 ; b.p. 58.8 ; m.p. −7.3° ; atomic weight 79.916 ; atomic number 35 ; solubility 3.6 gm. in 100 gm. water at 20° ; density 3.19 at 0°.

Bromine was discovered by Balard in 1826 by chlorinating the mother liquors (called **bittern**) left after the crystallisation of salt from sea water—these liquors contained magnesium bromide :

$$MgBr_2 + Cl_2 = MgCl_2 + Br_2.$$

Chief sources of bromine are : (i) *Sea water*—waters of the Atlantic ocean contains 0.007% of bromine, while the Dead Sea water contains 0.042% of the element, mainly as bromides. (ii) *Spring water*—spring waters in Ohio contain about 3.4—3.9% magnesium bromide, (iii) *Carnallite* of Stassfurt deposits in Germany, $KCl,MgCl_2,6H_2O$, contains about one per cent of magnesium bromide.

General method of Preparation of Halogens.—Chlorine, bromine or iodine may be obtained by heating the corresponding halide with manganese dioxide and concentrated sulphuric acid. The reaction is :

$MnO_2 + 2NaX + 3H_2SO_4 = MnSO_4 + 2NaHSO_4 + 2H_2O + X_2$. where $X = Cl$, Br or I. Fluorine cannot be prepared by this method.

Laboratory preparation of bromine.—A mixture of potassium bromide (5 gm.), manganese dioxide (15 gm.) and fairly strong sulphuric acid (100 c.c. 50% strength) is carefully heated in a stoppered glass retort, the end of which communicates with a water-cooled receiver (p. 40). Bromine distils and condenses as a dark red liquid in the receiver.

$$MnO_2 + 2KBr + 3H_2SO_4 = MnSO_4 + 2KHSO_4 + 2H_2O + Br_2.$$

Bromine may also be obtained by passing chlorine into a strong solution of potassium bromide : $2KBr + Cl_2 = 2KCl + Br_2$.

Properties.—(*i*) Bromine is a highly poisonous, *dark* red heavy **liquid** with irritating smell and corrosive properties—*the only non-metal which is liquid at the ordinary temperature.*

The bromine vapour attacks the eyes and the liquid corrodes the skin.

(ii) It dissolves in water (only 3.6% at 20°), giving a reddish-coloured solution, called **bromine water** which, though fairly stable in the dark, liberates nascent oxygen in bright sunlight.

$$2Br_2+2H_2O = 4HBr+O_2.$$

Bromine water on cooling yields red crystalline *bromine hydrate*, $Br_2,8H_2O$.

Bromine is readily soluble in such organic solvents as ether, alcohol, chloroform and carbon disulphide.

(iii) Bromine vapours (red in colour) do not burn but support the spontaneous combustion of many substances such as arsenic, antimony, phosphorus and potassium, yielding bromides.

Bromine directly unites with most metals and many non-metals yielding bromides, but *it is without action upon carbon, oxygen and nitrogen.*

Bromine is less active than chlorine but closely resembles it in chemical properties.

(iv) It reacts with hydrogen but less vigorously than chlorine. Bromine and hydrogen combine only when *heated ;* a burning jet of hydrogen burns in bromine vapour, yielding hydrogen bromide.

$$H_2+Br_2 = 2HBr.$$

(v) It resembles chlorine in its action upon caustic alkalis, yielding bromide and **hypobromite** with a cold solution of an alkali, and bromide and **bromate** with the hot alkali.

$$Br_2+2NaOH \text{ (cold)} = NaBr+NaOBr+H_2O.$$
$$3Br_2+6NaOH \text{ (hot)} = 5NaBr+NaBrO_3+3H_2O.$$

Bromine dissolves in alkaline hydrogen peroxide solution, evolving oxygen :

$$H_2O_2 + 2NaOH + Br_2 = 2NaBr + 2H_2O + O_2.$$

(vi) Like chlorine, it is an oxidising agent. Thus it precipitates sulphur from hydrogen sulphide, liberates iodine from hydrogen iodide, and converts sulphurous acid to sulphuric acid. It can displace iodine from potassium iodide : $2KI+Br_2 = 2KBr+I_2$.

$$H_2S+Br_2 = 2HBr+S \; ; \qquad 2HI+Br_2 = 2HBr+I_2.$$
$$H_2SO_3+Br_2+H_2O = H_2SO_4+2HBr.$$

(vii) Bromine water has feeble bleaching properties ; thus it bleaches litmus, and turns starch paper yellow.

(viii) Like chlorine, it gives addition products with unsaturated compounds : $C_2H_4+Br_2=C_2H_4Br_2$ (ethylene dibromide).

Tests.—Bromine is detected by its red colour and irritating smell ; it dissolves in carbon disulphide, giving reddish-brown solution. Bromine turns starch yellow.

Uses.—(i) In the manufacture of coal tar dyes and bromides (used in medicine and in photography) ; in the extraction of gold.

(ii) In the preparation of ethylene dibromide (used in anti-knock petrol) and methyl bromide (for fire extinguishers) and in many organic syntheses.

(iii) In making *tear gases ;* as a disinfectant and as an oxidising agent in the laboratory.

Bromine is kept in stoppered bottles. It severely corrodes the skin, which should be washed with petroleum if it comes in contact with bromine.

Iodine

Formula I_2. Atomic weight 126.92. Atomic number 53. Solubility in water at 0° 0.016% only. Density, 4.94. Melting point 113.9°. Boiling point 184.4°.

Laboratory preparation.—In the laboratory iodine is prepared by heating a mixture of potassium iodide, manganese dioxide and 50 per cent sulphuric acid in a stoppered glass retort (p. 40) which communicates with a water-cooled receiver. Iodine is liberated on heating the retort ; it sublimes as violet vapours and condenses in the receiver as black shining crystals :

$$MnO_2+2KI+3H_2SO_4 = MnSO_4+2KHSO_4+I_2+2H_2O.$$

Iodine may also be obtained by passing chlorine into a strong solution of potassium iodide : $2KI + Cl_2 = 2KCl + I_2$.

Sublimation of Iodine.—An intimately ground mixture of iodine (about 10 gms.) and potassium iodide (about 5 gms.) is carefully heated in a basin on a sand bath—a larger shallow dish filled with cold water, is placed on the top of the basin. On cautious heating, the bottom of the water-cooled dish becomes covered with shining crystals of iodine. The basin may also be covered with a funnel (p. 43) when iodine deposits on the inside wall.

Properties.—(i) Dark grey shining crystals ; the molecular formula of the vapour up to 700°C is I_2 but thermal dissociation occurs above 700°C : $I_2 \leftrightharpoons 2I$.

On dropping a few crystals of iodine in a heated flask, the latter is filled with violet vapours of iodine.

(ii) Very slightly soluble in water (1 part in 5000 parts), iodine readily dissolves in aqueous potassium iodide giving a brown solution, due to the formation of potassium tri-iodide : $KI+I_2 \leftrightharpoons KI_3$.

It is also freely soluble in organic solvents such as alcohol, chloroform, benzene, ether and carbon disulphide.

In water, ether and alcohol, iodine forms brown solutions, in benzene and chloroform purple solutions, and in carbon disulphide a violet solution.

Iodine resembles other halogens in chemical properties, but is much less active.

(iii) Iodine vapours do not burn, but very much like chlorine, they support the combustion of white phosphorus, arsenic, antimony, etc., though less energetically :

$$2P + 3I_2 = 2PI_3.$$

Iodine directly combines with most metals, but of the non-metals, it directly unites only with *hydrogen, phosphorus and the halogens*, yielding the *inter-halogen compounds* with the latter, namely, IF_5, IF_7, ICl, ICl_3, and IBr.

On rubbing mercury and iodine together in a mortar, a green mercurous iodide, Hg_2I_2 is formed if the mercury is in excess, and a red mercuric iodide, HgI_2, if the iodine is in excess : $Hg + I_2 = HgI_2$.

(iv) It has affinity for hydrogen ; but the affinity is much less compared to other halogens ; thus a mixture of hydrogen and iodine combines when heated in presence of a platinum catalyst, forming hydrogen iodide—*the reaction is reversible* : $H_2+I_2 \rightleftharpoons 2HI$.

(v) **Action on alkalis.**—It resembles chlorine in its reaction with alkalis—cold alkali giving iodide and **hypoiodite ;** hot alkali producing iodide and **iodate.** The hypoiodite rapidly passes into iodate and iodide on keeping.

$$I_2+2KOH = KI+KOI+H_2O \; ; \; 3I_2+6KOH = 5KI+KIO_3+3H_2O$$

Iodine dissolves in alkaline solution of hydrogen peroxide, giving off oxygen.

$$H_2O_2 + 2NaOH + I_2 = 2NaI + 2H_2O + O_2.$$

(vi) Iodine is a mild oxidising agent. Sulphur separates when hydrogen sulphide is passed into a suspension of iodine in water. It oxidises sulphurous acid to sulphuric acid, stannous chloride to stannic chloride, and arsenious acid to arsenic acid :

$$I_2 + H_2S = 2HI + S \; ; \quad H_2SO_3 + I_2 + H_2O = H_2SO_4+2HI.$$

$$H_3AsO_3 + I_2 + H_2O \rightleftharpoons H_3AsO_4 + 2HI.$$

(vii) Since iodine is practically insoluble in water, it has no bleaching properties.

(viii) **It gives a deep-blue colour with starch solution**—the colour disappears on heating and reappears on cooling.

(ix) It has no action upon potassium chloride or bromide, but chlorine or bromine can liberate iodine from potassium iodide, hence it is less active than these elements.

$$2KI + Cl_2 = 2KCl + I_2 \; ; \quad 2KI + Br_2 = 2KBr+ I_2.$$

Iodine can however liberate chlorine from potassium chlorate and chloric acid : $2KClO_3 + I_2 = 2KIO_3 + Cl_2$.

(x) Iodine reacts with sodium thiosulphate, $Na_2S_2O_3$, solution, yielding sodium tetrathionate and sodium iodide—a reaction used in estimating iodine (*iodometry*, as it is called).

$$2Na_2S_2O_3 + I_2 = Na_2S_4O_6 \text{ (sodium tetrathionate)} + 2NaI.$$

(xi) Unlike other halogens, iodine may be oxidised by concentrated nitric acid to iodic acid.

$$3I_2 + 10HNO_3 = 6HIO_3 + 10NO + 2H_2O.$$

Tests.—(i) Iodine yields violet vapours on heating. Iodine gives a blue colour with starch solution—1 part of iodine in 5,000,000 of water may be detected.

(ii) It dissolves in carbon disulphide, forming a violet solution.

(iii) It produces yellow crystals of iodoform of characteristic smell, when warmed with ethyl alcohol and caustic soda.

Chief sources of iodine are : (i) **Deep sea weeds** (*laminaria*)—Iodine does not occur free in nature ; sea-water contains traces of iodine—about 0.001 per cent—mainly as iodide ; this is absorbed by certain sea weeds. The sea weeds are drift ashore during storms. The ash of burnt sea-weed, called **kelp,** contains about one per cent combined iodine.

(ii) **Caliche.**—Crude Chile salt petre, called CALICHE, contains about 0.2 per cent sodium iodate and forms an important source of iodine.

(iii) **Petroleum brines.**—Californian brines, containing about 30—70 parts of iodine as iodide per million parts of it, is now one of the principal sources of iodine and has reduced the price of iodine by more than half.

Purification.—Crude iodine contains moisture and generally the impurities iodine chloride, ICl, iodine bromide, IBr, and iodine cyanide, ICN, which cannot be removed by sublimation, because of their volatility. These impurties are removed by heating a well ground mixture of crude iodine, lime (which retains moisture) and potassium iodide (which removes chlorine, bromine and cyanogen)—pure iodine sublimes :

$$ICl + KI = KCl + I_2.$$

Further purification is effected by dissolving the sublimed iodine in potassium iodide solution and then precipitating it by dilution with water —the precipitated iodine is finally dried in vacuo over conc. H_2SO_4.

Uses.—(i) In the manufacture of certain drugs, and dyes. Iodoform, CHI_3, is used as an antiseptic for dressing wounds.

(ii) As a disinfectant as **tincture of iodine** (solution of iodine in potassium iodide and rectified spirit—1 oz. each of KI, I_2 and water in one pint of rectified spirit).

(iii) In iodometry and organic syntheses. The practical use of iodometry is in the estimation of oxidising agents such as hydrogen peroxide which liberates iodine from an acidified solution of protassium iodide—the iodine being titrated with sodium thiosulphate, using starch as an indicator.

Iodine compounds also play an important part in the body—*thyroxin* is an iodine compound secreted by the thyroid gland ; goitre, a disease of the gland, is due to iodine deficiency. Use of table salt containing 0.023% KI is advocated to reduce the prevalence of goitre.

Hydrochloric acid [Muriatic acid] HCl

Formula HCl ; mol. wt. 36.465 ; b. p. −85°C ; m. p. −111.4 ; solubility per c.c. of water : 525 c.c. at 0°C and 458 c.c. at 15°C. The gastric juice contains aqueous solution of the acid (0.2—0.4 per cent).

Laboratory preparation.—Hydrochloric acid is prepared by gently heating common salt with concentrated sulphuric acid—the reaction is :

(i) $NaCl + H_2SO_4 = NaHSO_4 + HCl$ (150°—200°C.)

(ii) $NaCl + NaHSO_4 = Na_2SO_4 + HCl$ (over 500°C.)

The reaction (i) occurs on gentle warming, but the reaction (ii) does not take place until the temperature is raised to above 500°C.

Common salt is taken in a flask fitted with a thistle funnel and a delivery tube. Fairly concentrated sulphuric acid is poured down the funnel when a quick evolution of hydrogen chloride gas occurs. When this slackens, the flask is gently heated. The gas is dried by bubbling through concentrated sulphuric acid and collected by the upward displacement of air or over mercury.

If a solution of hydrogen chloride is required, the end of the delivery tube is connected with the stem of a funnel which dips just below the surface of water in a beaker—the gas dissolves in water, yielding an aqueous solution, (fig. 55).

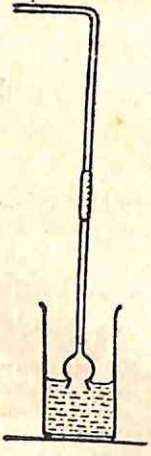


Fig. 55

Pure hydrogen chloride is obtained by the action of water upon silicon tetrachloride : $SiCl_4 + 4H_2O = Si(OH)_4 + 4HCl$.

A convenient supply of gas is readily obtained by dropping concentrated hydrochloric acid upon concentrated sulphuric acid taken in a flask.

Properties.—(i) A colourless gas with a choking smell and strongly fuming in moist air, hydrogen chloride is 1.27 times heavier than air ; it neither burns nor supports burning.

(ii) It is highly soluble in water. The solubility of the gas may be shown by *fountain experiment.*

A solution of the gas in water is known as hydrochloric acid. The saturated solution has a density of 1.231 at 15°C and contains 43 per cent hydrogen chloride.

Any solution of hydrochloric acid, on distillation, yields an ultimate residue of 20.24% hydrogen chloride, boiling at 110°C ; this is a *constant boiling mixture.*

(iii) In aqueous solution hydrogen chloride acts like a strong monobasic acid ; the solution readily dissolves base metals, liberating hydrogen and forming chlorides *containing the metal in the lowest (ous) state of valency :*

$$Sn + 2HCl = SnCl_2 + H_2 ; \quad Fe + 2HCl = FeCl_2 + H_2$$

The metals also react with hydrochloric acid gas, yielding anhydrous chloride—burning sodium continue burning in gaseous hydrocloric acid. Noble metals such as gold, platinum, etc., are not attacked by the acid. Copper slowly dissolves in hot and concentrated acid, and silver is slowly attacked *in presence of air only.*

$$2Cu+8HCl = H_2+2H_3CuCl_4 ; \quad 4Ag+4HCl+O_2 = 4AgCl+2H_2O.$$

Liquid hydrogen chloride does not conduct electricity and is without action upon metals in absence of water—aluminium, however, dissolves in it.

(iv) It reacts with metallic oxides and hydroxides, yielding salt and water : it combines with ammonia, in presene of trace of moisture, forming dense white fumes of ammonium chloride ; it decomposes carbonates, liberating carbon dioxide :

$$CuO+2HCl = CuCl_2+H_2O ; \quad NaOH+HCl = NaCl+H_2O.$$

$$NH_3+HCl = NH_4Cl ; \quad CaCO_3+2HCl = CaCl_2+H_2O+CO_2.$$

(v) It is readily oxidised to chlorine by manganese dioxide or potassium permanganate. $MnO_2+4HCl = MnCl_2+2H_2O+Cl_2$.

Tests.—(i) Heated with manganese dioxide and concentrated sulphuric acid, hydrogen chloride or any metallic chloride, yields the greenish yellow gas chlorine.

(ii) In aqueous solution hydrogen chloride or any soluble metallic chloride gives a curdy white precipitate of silver chloride with silver nitrate solution—the precipitate is soluble in ammonia but insoluble in nitric acid.

$$HCl + AgNO_3 = HNO_3 + AgCl ; \quad AgCl + 2NH_3 = [Ag(NH_3)_2]Cl.$$

Uses.—Hydrochloric acid stands second only to sulphuric acid in its uses in industry. It is used : (i) in making metallic chlorides, (ii) in dyeing and calico-printing and in medicine, (iii) in pickling baths to remove oxide scale from sheet iron which is to be tinned, galvanised or made into enamel ware, (iv) in making glue from cartilage, and glucose from starch. Hydrochloric acid is a reagent in the laboratory. It is used in aqua regia to dissolve gold and platinum. C.P. (chemically pure) concentrated acid contains 37.58 to 38.95 per cent HCl and has a density of 1.190 to 1.196.

Composition of hydrogen chloride.—The composition of hydrogen chloride may be determined either by *analysis* or by *synthesis*.

(i) **By analysis.**—(a) When a concentrated aqueous solution of hydrochloric acid is electrolysed, chlorine is liberated at the anode and hydrogen at the cathode.

A dilute solution of acid, it must be remembered, yields hydrogen and oxygen, on electrolysis.

The electrolysis is carried out in a three-limbed voltameter—the central tube carrying a funnel acts as the reservoir of the acid and the two graduated side-tubes, fitted with *gascarbon electrodes* (chlorine attacks platinum) at the bottom, are the collecting vessels (fig. 56). The apparatus is filled with the acid through the funnel and the electrolysis carried out by connecting the carbon electrodes with the poles of a battery. Hydrogen collects at the cathode but the chlorine liberating at the anode, dissolves in water, *until the solution is saturated with chlorine*—very little chlorine collects at the anode before saturation. The hydrogen, collected at the cathode, is allowed to pass out and the apparatus is then filled with the solution thus saturated with chlorine and the process of electrolysis continued. It is found that hydrogen and chlorine collect in equal volumes in the two limbs. Hence *hydrochloric acid contains equal volumes of hydrogen and chlorine.*

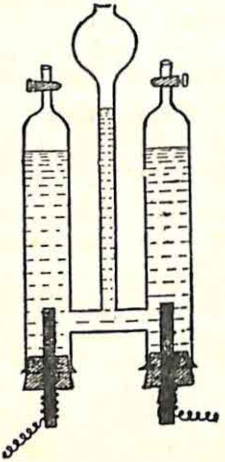


Fig. 56

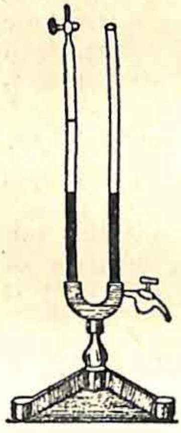


Fig. 57

(b) Hydrogen chloride may be shown to contain half its volume of hydrogen by its reaction with sodium amalgam. A measured volume of hydrogen chloride is collected in a graduated tube over mercury (fig. 57) and a pellet of sodium amalgam introduced into it. The reaction over, mercury stands at half its original volume—the residual gas in the tube is found to be hydrogen. Hence hydrogen chloride contains half its volume of hydrogen.

Sodium-amalgam + 2HCl = sodium chloride + H_2.

But the hydrogen chloride gas contains equal volumes of hydrogen and chlorine. Hence 2 volumes of hydrogen chloride = 1 volume of hydrogen + 1 volume of chlorine.

(ii) **By Synthesis.**—A glass tube (fig. 58) provided with stop-cocks at the two ends is made into two equal halves by a three way stop-cock. The two halves are filled with hydrogen and chlorine, one gas in each half. The gases are mixed by opening the central tap and the mixture exposed to diffused sun-light for about two days. On opening one of the end stop-cocks under mercury, *no change of volume takes place*; but when opened under water, it rushes up and completely fills the tube, showing that there is no uncombined hydrogen. The aqueous solution does not liberate iodine from potassium iodide and hence contains no free chlorine; the solution is found to be acidic and yields a white precipitate with silver nitrate and hence it is hydrochloric acid. This shows that the whole of hydrogen and chlorine have combined and the gas obtained after the reaction consists of hydrogen chloride only. Hence :

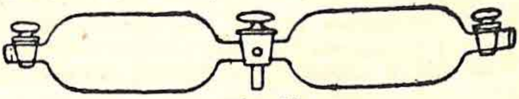


Fig. 58

2 vols. hydrogen chloride = 1 vol. hydrogen + 1 vol. chlorine.

Or, 2 mols. hydrogen chloride = 1 mol. hydrogen + 1 mol. chlorine.
(By Avogadro's hypothesis).

Or, 1 mol. hydrogen chloride = $\frac{1}{2}$ mol. or 1 atom of $H_2 + \frac{1}{2}$ mol or 1 atom of Cl_2.

Hence, the formula of hydrogen chloride is HCl. This agrees with the molecular weight 36.5 arrived at experimentally from its vapour density.

Comparison of the Properties of halogens

Physical properties	*Fluorine*	*Chlorine*	*Bromine*	*Iodine*
(i) Atomic number	9	17	35	53
(ii) Atomic weight	19	35.457	79.916	126.91
(iii) Colour and form	Pale yellow gas	Greenish yellow gas	Dark red liquid ; gives off red vapours	Grey lustrous solid ; gives off violet vapours on heating
(iv) Smell	Irritating	Irritating	Extremely irritating	Irritating smell of vapour
(v) Specific gravity	1.11 (liquid at boiling point)	1.55 (liquid at boiling point)	3.19 (liquid at 0°C)	4.94 (solid at 18°C)
(vi) Melting point °C	−223°	−102°	−7°	+114°
(vii) Boiling point	−187°	−34°	+59°	+184°
(viii) Solubility in water at 0°	Decomposes water	14.6 gms. per litre	41.5 gms. per litre	0.162 gm. per litre
Chemical properties				
(i) Whether combustible or not	Fluorine inflames in hydrogen, otherwise non-combustible	Chlorine burns in hydrogen, otherwise non-comoustible	Non-combustible	Non-combustible
(ii) If supporter of combustion	As, S, P, Na, K, etc. spontaneously catch fire in the gas, forming their fluorides.	As, Sb, P, Cu, etc. spontaneously ignite in the gas. Heated sodium also burns in the gas.	As, Sb, P, etc. spontaneously burn in the bromine vapours	Iodine vapours support combustion of As, Sb, P etc. ; but less energetically
(iii) Reaction with hydrogen. Affinity for H_2 decreases from F_2 to I_2	Explosive even in the dark, forms HF even at −252°.	Explosive in sunlight ; froms HCl ; no reaction in the dark	Forms HBr in contact with heated platinum	Slowly forms HI in contact with heated platinum
(iv) Action on metals, forming halides	Attacks all metals—most metals burn, e.g., Na, K.	Attacks all metals—many metals burn, e.g., Na	Attacks most metals—a few only burn, e.g. K.	Attacks most metals except platinum.
(v) Action on non-metals, forming halides.	Combines directly with all except N_2 and O_2.	Combines directly with all except C, N_2 and O_2.	Combines directly with all except C, Si, N_2 and O_2.	Combines directly with halogens, hydrogen, P and As.

Chemical properties	*Fluorine*	*Chlorine*	*Bromine*	*Iodine*
(vi) Action on water	Decomposes water, forming HF, O_3 and a little ozone.	Dissolves to form chlorine water, which evolves O_2 in sunlight : $Cl_2+H_2O=HCl+HOCl$ $=2HCl+O$ Also directly decomposes water in sunlight : $Cl_2+H_2O \rightleftharpoons 2HCl+O$	More soluble than Cl_2 ; bromine water slowly liberates O_2 in sunlight $Br_2+H_2O=2HBr+O$	Slightly soluble in water. Freely soluble in water containing KI in solution.
(vii) Reactivity ; reactivity decreases from F_2 to I_2	Most reactive ; liberates Cl, Br, and I respectively from HCl, HBr, HI and their salts.	Less reactive than fluorine ; liberates Br and I respectively from HBr, HI and their salts	Less reactive than chlorine ; liberates iodine from HI and its salts	Least reactive, cannot liberate F, Cl, and Br from HF, HCl, HBr and their salts.
(viii) Reaction with caustic alkali :				
(a) Cold solution	(a) Forms F_2O with cold dilute alkali but evolves O_2 with concentrated alkali.	(a) Forms chloride and *hypochlorite*	(a) Forms bromide and *hypobromite*	(a) Forms iodide and *hypoiodite*
(b) Hot solution	(b) *No oxyacids and oxy salts are formed.*	(b) Forms chloride and *chlorate*	(b) Forms bromide and *bromate*	(c) Forms iodide and *iodate*
(ix) Oxidising action	Vigorous oxidising agent	Strong oxidising agent $H_2S+Cl_2=2HCl+S$	Oxidising agent $H_2S+Br_2=2HBr+S$	Feeble oxidising agent $H_2S+I=2HI+S$
(x) Bleaching action	Destroys the material	Readily bleaches in presence of moisture	Slowly bleaches in presence of moisture	No bleaching action
(xi) Action on starch solution	Attacks the solution	No change of colour	Yellow coloration	Blue coloration
(xii) Action of oxidising agent	No action Indirectly forms F_2O and F_2O_2	No action Indirectly forms Cl_2O, ClO_2, Cl_2O_6 and Cl_2O_7	Oxidised to Br_3O_8 by ozone. Indirectly forms Br_2O and BrO_2	Oxidised by ozone and also by nitric acid to iodic acid. Forms the oxides I_2O_4, I_2O_5 and I_4O_9.

Comparison of the Properties of Halogens.—The halogens fluorine, chlorine, bromine, and iodine form a family of closely related elements. Their properties show a regular gradation with increasing atomic weights from fluorine to iodine.

The halogens do not occur in the free state. They are monovalent and form univalent anion in their halides, e.g., NaF, NaCl, NaBr and NaI.

(i) The melting and boiling points as well as the density of the halogens gradually increase from fluorine to iodine ; the state of existence of the halogens also shows a gradation from gas to solid with deepening of colour.

(ii) The halogens are the **most electro-negative** (non-metallic) elements—the non-metallic character gradually decreasing from fluorine to iodine. As non-metals, they exhibit great **affinity for hydrogen and metals,**—the affinity, however, gradually decreasing from fluorine to iodine.

(iii) The halogens are very reactive chemically. The *reactivity* decreases in general with decreasing electro-negativeness ; thus fluorine can displace chlorine from its salts, chlorine can displace bromine, and bromine can displace iodine.

(iv) **Oxidising and bleaching action.**—The halogens are powerful oxidising agents—their oxidising power diminishing with decreasing electro-negativeness. The bleaching property decreases from chlorine to iodine which does not bleach at all—fluorine destroys the material to be bleached.

(v) **Affinity for oxygen.**—The affinity for oxygen (unlike that for hydrogen) generally increases from fluorine to iodine. Iodine is directly oxidised to iodic acid by hot concentrated nitric acid. A large number of oxides of halogens have been obtained by *indirect means*.

(vi) **Action of alkali.**—Fluorine differs from other halogens in not forming oxysalts with alkalis—with cold dilute alkali, it reacts, yielding fluorine monoxide, F_2O, while with hot concentrated alkali oxygen is liberated. Chlorine, on the other hand, reacts with cold dilute alkali, producing chloride and hypo-chlorite ; with hot concentrated alkali it yields chloride and chlorate. Bromine and iodine behave like chlorine.

Exercises

1. Describe the preparation of a sample of chlorine free from hydrogen chloride. State its chief properties and uses. Explain, with equations, the action of chlorine upon—(*a*) milk of lime, (*b*) sulphurous acid, (*c*) hydrogen sulphide, (*d*) molten tin, (*e*) slaked lime. *P. U.* 1961.

2. What are the chief sources of bromine ? How is bromine prepared in the laboratory. State its chief properties and uses. Describe the reactions of bromine with (*i*) phosphorus, (*ii*) sulphur dioxide, (*iii*) caustic soda, (*iv*) potassium iodide, (*v*) ethylene. *Calcutta* '53.

3. What are the chief sources of iodine ? How is iodine prepared and purified in the laboratory ? State its chief properties and uses. Describe and explain the actions of iodine on (*a*) mercury, (*b*) nitric acid, (*c*) sodium thiosulphate, (*d*) hydrogen sulphide, (*e*) potassium iodide, (*f*) caustic soda, (*g*) iron filings. *Calcutta* '57.

4. How is hydrochloric acid made in the laboratory and for what purposes is it used ? How would you establish that its formula is HCl ? State its properties, tests and uses

5. Compare the physical and chemical properties of the halogens. *Punjab* '34.

6. Iodine resembles graphite in appearance. How would you distinguish between them ? Explain how you would separate a mixture of iodine and potassium iodide.

Describe what happens when : (*a*) a crystal of iodine is heated in a flask.

(*b*) chlorine water is added to potassium iodide solution, and then shaken with carbon disulphide.

(*c*) a crystal of iodine is shaken with potassium iodide solution.

(*d*) iodine is heated with concentrated nitric acid.

7. Explain how chlorine bleaches. Give examples to illustrate it. Describe the action of chlorine with (*a*) oil of turpentine, (*b*) aqueous solution of ferrous chloride, (*c*) hot caustic potash solution, (*d*) a solution of potassium iodide, (*e*) hydrogen, (*f*) heated iron wire, and (*g*) water. How would you know that sodium chloride contains chlorine ?

8. Explain what happens when : (*i*) a jet of burning hydrogen is introduced into a jar of chlorine, (*ii*) dry chlorine is passed over molten tin, (*iii*) chlorine is passed into ferrous sulphate acidified with sulphuric acid, (*iv*) an aqueous solution of chlorine is exposed to sunlight, (*v*) a mixture of hydrogen and chlorine is exposed to sunlight, (*vi*) chlorine is passed into hot caustic potash solution until saturated, (*vii*) common salt is heated with manganese dioxide and sulphuric acid, (*viii*) chlorine is led into a jar containing molten phosphorus under water.

XV

SULPHUR AND ITS COMPOUNDS

Huge deposits of sulphur occur in volcanic regions of Sicily, Japan, and in Louisiana and Texas.

Combined sulphur occurs as metallic sulphide and *sulphates* ; the more important sulphides are : *galena*, PbS ; *zinc blende*, ZnS ; *copper pyrites*, Cu_2S, Fe_2S_3 ; *cinnaber*, HgS ; and *Iron pyrites*, FeS_2. The sulphates are : *gypsum*, $CaSO_4$, $2H_2O$; *anhydrite*, $CaSO_4$; *heavy spar*, $BaSO_4$ and kieserite, $MgSO_4$, H_2O.

Sulphur occurs in many organic matter, for example, in hair, egg albumen, in odorous principles of garlic, onion and mustard.

Allotropy of sulphur.—Many allotropic forms of sulphur exist which differ markedly in their physical properties. The two common *crystalline* forms : (i) *rhombic* or α-sulphur, (ii) *monoclinic* or β-sulphur, and the three amorphous forms : (i) *plastic* or γ-sulphur, (ii) *milk of sulphur*, (iii) *colloidal sulphur*.

Rhombic sulphur.—It is best prepared by slowly evaporating a solution of roll sulphur in carbon disulphide—transparent lemon-yellow octahedral crystals (fig. 23) deposit, density 2.06 ; its m.p. is 112.8. *It is soluble in* CS_2. It is the most stable form at ordinary temperature—most other forms pass into it on keeping. Its formula is S_8.

Monoclinic sulphur.—It is *soluble in carbon disulphide*—the solution on evaporation yields sulphur. Its m.p. is 118.75° and density 1.96. Its formula is S_8. Unstable at ordinary temperature, it passes into rhombic form on standing.

It is experimentally found that above 95.5° monoclinic sulphur is stable, and below 95.5° rhombic sulphur is stable, while at 95.5° both the forms are stable and remain in equilibrium—this is the **transition temperature** for the two crystalline forms of sulphur : $S\,\alpha \rightleftharpoons S\beta$. The transformation is reversible.

Monoclinic or β-sulphur is prepared by allowing fused sulphur to cool slowly. A large porcelain crucible is nearly filled with pieces of roll sulphur, and *gently* heated on a sand bath until the whole of sulphur is just fused. It is then allowed to cool until a crust is formed on the surface. The crust is pierced at two points with a pointed glass rod, and the still liquid sulphur is poured out. On removing the surface crust, transparent yellow needle-shaped crystals of β-sulphur, also called **prismatic sulphur,** are found inside the crucible (fig. 24).

Plastic sulphur.—Small pieces of roll sulphur are heated in a large test tube until they melt to a clear mobile liquid. When this liquid sulphur, heated nearly to its boiling point, is poured in a thin stream in cold water, it solidifies to rubber-like elastic, transparent yellow threads, called *plastic sulphur* or γ-sulphur, density 1.92.

It is insoluble in carbon disulphide. It passes into rhombic form on standing. Plastic sulphur consists of chain of sulphur atoms and hence it can be stretched.

Milk of Sulphur.—This is a variety of white amorphous sulphur. Powdered roll sulphur when boiled with milk of lime dissolves, forming calcium pentasulphide and thiosulphate ; the orange-yellow liquid is filtered and acidified with dilute hydrochloric acid when milk of sulphur is deposited.

$$12S + 3Ca(OH)_2 = 2CaS_5 + CaS_2O_3 + 3H_2O.$$

$$2CaS_5 + CaS_2O_3 + 6HCl = 3CaCl_2 + 12S + 3H_2O.$$

Milk of sulphur is soluble in carbon disulphide, and is used in medicine. It passes into rhombic sulphur on heating.

Colloidal Sulphur.—A turbid and milky colloidal suspension of sulphur is prepared by acidifying a solution of sodium thiosulphate or by passing hydrogen sulphide into a solution of sulphur dioxide :

$$Na_2S_2O_3 + H_2SO_4 = Na_2SO_4 + H_2O + SO_2 + S$$

$$2H_2S + SO_2 = 2H_2O + 3S.$$

The addition of little alum coagulates colloidal sulphur. Some forms of colloidal sulphur are *soluble in carbon disulphide*, and others insoluble. It is used medicinally.

Uses of Sulphur.—(i) Huge quantities of sulphur are burnt to sulphur dioxide, which is either converted to sulphuric acid or to calcium bisulphite which is used in paper-making ;

(ii) Sulphur is also used for making carbon disulphide, sulphur chloride, sodium thiosulphate, ultrammarine, gunpowder, matches, dyes, and in vulcanising rubber and in fire works.

(iii) It finds use in medicine, and as a *fungicide in agriculture* in vineyards.

Properties of sulphur.—(i) Sulphur is a pale yellow brittle solid, non-conductor of heat and electricity, and boils at 444.6°—the temperature is definite to be used as a fixed point in thermometry. Sulphur is insoluble in water. Crystalline sulphur dissolves in carbon disulphide and in hot benzene and turpentine—plastic sulphur is insoluble in carbon disulphide.

(ii) It burns with a pale blue flame in air or oxygen, forming sulphur dioxide mainly and a little sulphur trioxide. $S+O_2 = SO_2$.

(iii) It directly unites, under the influence of heat with hydrogen, halogens (except iodine), carbon, phosphorus and most metals, forming sulphides.

$$H_2 + S = H_2S \; ; \quad Cu + S = CuS$$

$$S + 3F_2 = SF_6 \; ; \quad 2S + Cl_2 = S_2Cl_2$$

(iv) Hot concentrated sulphuric and nitric acids oxidise sulphur to sulphur dioxide and sulphuric acid respectively.

$S+2H_2SO_4 = 3SO_2+2H_2O$; $S+6HNO_3 = H_2SO_4+6NO_2+2H_2O$.

(v) Sulphur dissolves in hot alkali giving sulphide and thio-sulphate ; the sulphide combines with more sulphur, forming poly-sulphide, such as K_2S_2.

$4S+6KOH = 2K_2S+K_2S_2O_3$ (potassium thiosulphate) $+3H_2O$.

Hydrogen sulphide or Sulphuretted hydrogen, H_2S.

Occurrence.—Hydrogen sulphide is found in volcanic gases and in many spring waters. As a product of putrefaction of sulphur-containing material, it is present in sewer gas. The unpleasant smell of putrefied hides and rotten eggs is partly due to this gas. The atmosphere usually contains a trace of it, which causes silver object to tarnish owing to the formation of a film of black silver sulphide.

Laboratory preparation.—Hydrogen sulphide is usually prepared in the laboratory by the action of cold dilute sulphuric acid (1 vol. acid and 6 vols. water) upon pieces of ferrous sulphide taken in a Woulf's bottle fitted with a thistle funnel and a delivery tube—the gas is collected *by the upward displacement of air.* The gas may be washed with a little water and collected over hot water, if it is not required dry. It may be dried with fused calcium chloride or phosphorus pentoxide, (but *not with concentrated sulphuric acid which is reduced to sulphur dioxide :* $H_2SO_4+H_2S = 2H_2O+SO_2+S$) and then collected in dry jars by the displacement of air.

$$FeS+H_2SO_4 = FeSO_4+H_2S.$$

Ferrous sulphate is obtained as a by-product. Kipp's apparatus is used to obtain a ready supply of the gas for use in the laboratory.

Unless dry and free from oxygen, the hydrogen sulphide attacks mercury and tarnishes it.

Purification.—(i) Besides acid spray, the gas so prepared always contains some hydrogen evolved by the action of the acid upon free iron, invariably present in ferrous sulphide which is made by fusing iron and sulphur together. The gas is freed from acid spray by passing through a saturated solution of sodium hydrogen sulphide, $NaHS + HCl = NaCl + H_2S$, and from moisture by phosphorus pentoxide, and then cooled with solid carbon dioxide, when hydrogen sulphide liquefies and hydrogen passes out.

(ii) The impure gas is passed into a suspension of magnesium oxide in water, when only hydrogen sulphide is absorbed forming magnesium hydro-sulphide which evolves pure H_2S on heating to 60°C.

$$MgO + 2H_2S \leftrightharpoons Mg(HS)_2 + H_2O.$$

Pure hydrogen sulphide free from hydrogen is prepared by the action of hot concentrated hydrochloric acid upon antimony sulphide. The gas is washed with water to remove hydrochloric acid and dried over phosphorus pentoxide.

$$Sb_2S_3 + 6HCl = 2SbCl_3 + 3H_2S.$$

The purest hydrogen sulphide is best obtained by passing hydrogen and sulphur vapour over finely divided nickel at 450° : $H_2 + S \leftrightharpoons H_2S$

Properties.—(i) A colourless, heavier-than-air gas, with the smell of rotten eggs, hydrogen sulphide is very poisonous in concentration above 0.1 per cent ;

(ii) It does not support combustion, but it burns with a blue flame in excess of air or oxygen, giving water and sulphur dioxide; but sulphur is deposited, if the supply of oxygen is limited—hence the *presence of sulphur* in the gas. The gas is also oxidised to sulphur, when mixed with air and passed over heated iron oxide :

$$2H_2S+3O_2 = 2H_2O+2SO_2\ ;\quad 2H_2S+O_2 = 2H_2O+2S.$$

(iii) It is fairly soluble in cold water—the solution is a *weak dibasic acid* which reacts with alkali, giving sulphide and hydro-sulphide :

$$H_2S+2NaOH = Na_2S+2H_2O\ ;\quad H_2S+NaOH = NaHS+H_2O$$

Left in contact with air, the solution of hydrogen sulphide becomes turbid due to the separation of sulphur by atmospheric oxidation.

$$2H_2S + O_2 = 2H_2O + 2S.$$

(iv) *Hydrogen sulphide is a reducing agent :*

(a) When hydrogen sulphide is passed into chlorine or bromine water, or into iodine suspended in water, sulphur is deposited and the halogens are reduced to their hydracids :

$$Cl_2+H_2S = 2HCl+S\ ;\quad I_2+H_2S = 2HI+S.$$

(b) Hydrogen sulphide reduces sulphur dioxide in presence of moisture : $SO_2+2H_2S = 2H_2O+3S.$

(c) Hydrogen sulphide reduces ferric salts to ferrous salts; thus it reduces yellow ferric chloride solution into colourless ferrous chloride, sulphur being deposited :

$$2FeCl_3+H_2S = 2FeCl_2+2HCl+S.$$

(d) It reduces *pink* solution of potassium permanganate acidified with dilute sulphuric acid to a colourless solution, with deposition of sulphur. It also reduces potassium dichromate solution acidified with dilute sulphuric acid—the orange-red colour of the solution turning green, with precipitation of sulphur :

$$2KMnO_4 + 3H_2SO_4 + 5H_2S = K_2SO_4 + 2MnSO_4 + 8H_2O + 5S.$$

$$K_2Cr_2O_7 + 4H_2SO_4 + 3H_2S = K_2SO_4 + Cr_2(SO_4)_3 + 7H_2O + 3S.$$

(e) Sulphur is deposited when hydrogen sulphide is passed into concentrated sulphuric acid, and *hence the latter is not used in drying the gas*. It also reduces nitric acid, sulphur being deposited, and hence *the acid is not used in the preparation of the gas :*

$$H_2SO_4+H_2S = 2H_2O+SO_2+S\ ;\ 2HNO_3+H_2S = 2H_2O+2NO_2+S.$$

(v) The gas is decomposed into its elements under the influence of electric sparks or when passed through a red-hot tube.

Metallic sulphides.—Hydrogen sulphide is used **as a reagent in qualitative analysis.** The gas precipitates sulphides of many metals with characteristic colours from solutions of their salts. Many sulphides are precipitated from solutions *acidified* with dilute hydrochloric acid—copper, lead, mercury and bismuth salts, all give black sulphide; cadmium and arsenic give *yellow sulphide ; antimony*, an orange-yellow sulphide; tin (stannous), a brown sulphide.

$$CuSO_4+H_2S = H_2SO_4+CuS\ ;\quad HgCl_2+H_2S = 2HCl+HgS$$

$$CdCl_2+H_2S = 2HCl+CdS\ ;\quad SnCl_2+H_2S = 2HCl+SnS$$

Many sulphides are precipitated only in *alkaline solution ;* in ammoniacal solution zinc salts give a *white* sulphide ; manganese, a *flesh-coloured* sulphide ; iron, cobalt and nickel, all give *black* sulphide.

$$ZnSO_4+(NH_4)_2S = ZnS+(NH_4)_2SO_4 ;$$
$$FeSO_4+(NH_4)_2S = FeS+(NH_4)_2SO_4 ;$$

Sulphides of alkali metals are soluble in water ; sulphides of alkaline earth metals are sparingly soluble, but they react with water giving solube hydrosulphides : $2CaS+2H_2O = Ca(HS)_2+Ca(OH)_2$; aluminium and chromium sulphides are decomposed by water forming the hydroxide :

$$Al_2S_3+6H_2O = 2Al(OH)_3+3H_2S.$$

Metallic Sulphides
- Soluble in water. Sulphides of alkali and alkaline earth metals.
- Insoluble in water
  - Soluble in dil. HCl but insoluble in ammonium hydroxide—sulphides of Fe, Co, Ni, Zn and Mn.
  - Insoluble in dil. HCl—sulphides of Hg, Pb, Bi, Cu, Cd, As, Sn and antimony.

H_2S is generally used **as a reagent in qualitative analysis** for :

(i) **the identification of metals** from the distinctive colours of their sulphides ;

(ii) **the classification of metals** into groups according to the solubility of metallic sulphides in water, acid and alkali ; and

(iii) **the separation of metals** of different groups from a solution of their salts—thus when hydrogen sulphide is passed into a hot solution, containing salts of *copper*, *zinc and sodium*, and acidified with dilute hydrochloric acid, only black copper sulphide precipitates which is separated by filtration. On passing H_2S into the filtrate, made alkaline with ammonia, white zinc sulphide precipitates, the sodium salt remains in solution.

Tests.—Hydrogen sulphide is recognised (i) by its smell of rotten eggs, (ii) in its staining silver coin black due to formation of a film of silver sulphide, (iii) by its turning lead acetate paper *black* due to the formation of lead sulphide, $Pb(CH_3COO)_2 + 2H_2S = PbS + 2CH_3COOH$, and (iv) by the production of *purple colour* with alkaline sodium nitroprusside solution—alkali sulphide solution (but not free hydrogen sulphide) responds to this test.

The presence of sulphide in insoluble sulphides is detected by reduction with nascent hydrogen (heating the sulphide with zinc and strong hydrochloric acid) when hydrogen sulphide evolves, which turns lead acetate paper black. Alternatively, the sulphide is fused with sodium carbonate and the mass extracted with water—the extract gives a purple colour with sodium nitroprusside solution.

Hydrogen sulphide may be prepared in the laboratory by heating an intimate mixture of sulphur, paraffin and shredded asbestos.

Absorbent.—An acidic gas H_2S is absorbed by the caustic alkalis, NaOH and KOH ; lead nitrate solution also absorbs the gas.

$$Pb(NO_3)_2 + H_2S = 2HNO_3 + PbS \text{ (black precipitate).}$$

Oxides and oxyacids of sulphur.—Two important oxides of sulphur with their corresponding oxyacids are :

Sulphur dioxide, SO_2	Sulphurous acid, H_2SO_3
Sulphur trioxide, SO_3	Sulphuric acid, H_2SO_4.

Sulphur dioxide, SO_2 b.p. $-10.0°$; m.p. $-72°$; critical temperature 157.2°. Solubility in water, 45 vols, in 1 vol. H_2O at 15°C.

Laboratory Preparation.—The gas is prepared in the laboratory by reducing concentrated sulphuric acid with copper. Copper turnings are taken in a flask (fig. 59) fitted with a thistle funnel and a delivery tube. Concentrated sulphuric acid is poured down the funnel to cover the copper, and the flask is then slowly heated till sulphur dioxide is evolved with effervescence. The gas is collected *by upward displacement of air.* It may be dried by concentrated sulphuric acid, calcium chloride or phosphorous pentoxide, and collected over mercury.

$$2H_2SO_4+Cu = CuSO_4+2H_2O+SO_2.$$

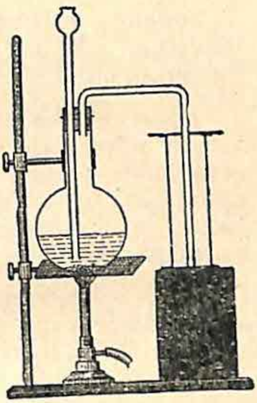


Fig. 59

Concentrated sulphuric acid may also be reduced to sulphur dioxide by heating with mercury, silver, sulphur or charcoal.

$$Hg + 2H_2SO_4 = HgSO_4 + 2H_2O + SO_2 ;$$
$$2Ag + 2H_2SO_4 = Ag_2SO_4 + 2H_2O + SO_2.$$
$$S + 2H_2SO_4 = 3SO_2 + 2H_2O ; \quad C + 2H_2SO_4 = 2SO_2 + 2H_2O + CO_2.$$

The gas is readily obtained without heating by dropping concentrated sulphuric acid into a solution of sodium hydrogen sulphite :

$$NaHSO_3 + H_2SO_4 = NaHSO_4 + H_2O + SO_2.$$

Industrial preparation.—Sulphur dioxide is obtained industrially by burning sulphur in air. The gas is dissolved out from the products of combustion by a descending stream of cold water in a tower. The sulphur dioxide is boiled out of the resulting solution, dried by refrigeration and concentrated sulphuric acid, liquefied under pressure, and stored in steel cylinders.

It may also be obtained by roasting *sulphide minerals,* such as iron pyrites, copper pyrites, and zinc blende, or *spent iron oxide.*

$$4FeS_2 + 11O_2 = 2Fe_2O_3 + 8SO_2 ; \quad 2ZnS + 3O_2 = 2ZnO + 2SO_2.$$

The gas (mixed with CO_2 and nitrogen) is obtained now-a-days by heating gypsum with clay, sand and coke, and is used for making sulphuric acid.

Properties.—(i) A colourless, heavier-than-air gas with a choking smell of burnt sulphur, sulphur dioxide is easily liquefied by pressure (2.5 atmosphere at 15°) or by cooling in a freezing mixture.

(ii) An incombustible gas, it does not support the combustion of hydrogen or a lighted taper, but heated potassium, tin, iron, and magnesium burn in the gas.

$$4K+3SO_2 = K_2SO_3+K_2S_2O_3 \text{ (potassium thiosulphate).}$$

(iii) It is highly soluble in water—the solution smells strongly of the gas and is *acidic* due to the formation of unstable *sulphurous* *acid*, $H_2O+SO_2 \rightleftharpoons H_2SO_3$, known in solution only—the acid is dibasic and forms *acid sulphites*, also called *bisulphites*, such as $NaHSO_3$, and normal sulphites such as Na_2SO_3. The sulphur dioxide is expelled from its solution by boiling.

(iv) *An acidic oxide*, it is *absorbed* by alkalis to yield bisulphites and sulphites :

$$NaOH+SO_2 = NaHSO_3 \text{ ; } NaHSO_3+NaOH = Na_2SO_3+H_2O.$$

Sodium carbonate solution reacts similarly, yielding sodium bisulphite, which then reacts with more sodium carbonate to form sodium sulphite : $Na_2CO_3+H_2O+2SO_2 = 2NaHSO_3+CO_2$.

$$2NaHSO_3+Na_2CO_3 = 2Na_2SO_3+CO_2+H_2O.$$

(b) Sulphur dioxide turns lime water milky due to the formation of insoluble calcium sulphite, which dissolves (and hence the milkiness disappears) in excess of the gas, yielding calcium bi-sulphite : (cf. CO_2). Milk of lime reacts similarly, yielding calcium bi-sulphite.

$$Ca(OH)_2+SO_2 = CaSO_3+H_2O; CaSO_3+H_2O+SO_2 = Ca(HSO_3)_2$$

(v) *It is a reducing agent.*—A solution of sulphur dioxide or sulphite slowly absorbs oxygen from the air to form sulphuric acid, the reaction is catalysed by trace of copper or iron salts. Chlorine, bromine or iodine oxidise it immediately to sulphuric acid.

$$2H_2SO_3+O_2 = 2H_2SO_4 \text{ ; } Cl_2+SO_2+2H_2O = H_2SO_4+2HCl.$$

It *decolorises* an acidified solution of potassium permanganate by reduction. It reduces an acidified solution of potassium dichromate the colour of the solution changing from *orange-yellow to green.*

$$2KMnO_4+5SO_2+2H_2O = K_2SO_4+2MnSO_4+2H_2SO_4.$$

$$K_2Cr_2O_7+3SO_2+H_2SO_4 = K_2SO_4+Cr_2(SO_4)_3+H_2O.$$

Sulphur dioxide is readily oxidised by hydrogen peroxide:

$$H_2O_2+H_2SO_3 = H_2O+H_2SO_4$$

It reduces ferric salts to ferrous salts :

$$2FeCl_3 + SO_2 + 2H_2O = 2FeCl_2 + 2HCl + H_2SO_4$$

(vi) *Oxidising action of sulphur dioxide.*—It oxidises moist hydrogen sulphide to sulphur : $2H_2S+SO_2 = 2H_2O+.3S$.

In strongly acid solution sulphur dioxide oxidises ferrous chloride :

$$4FeCl_2 + 4HCl + SO_2 = 4FeCl_3 + 2H_2O + S.$$

(vii) Sulphur dioxide possesses *bleaching properties in presence* of moisture. *Moist* coloured flowers are bleached colourless by sulphur dioxide, but not the *dry flowers*. Magenta solution is decolorised by the gas, but not litmus. The bleaching is due to the reduction of the colours to colourless compounds by nascent hydrogen, thus :

$$\text{Colouring matter} + H_2O + H_2SO_3 = \text{Colourless reduction product} + H_2SO_4.$$

Bleaching properties of sulphur dioxide and chlorine.—(a) *Sulphur dioxide bleaches by reduction* (cf. *chlorine which bleaches in presence of moisture by oxidation*).

(b) *Sulphur dioxide is a milder bleaching agent than chlorine*, and hence delicate fabrics, such as wool, silk, straw for hats, etc., which are likely to be injured by chlorine, are bleached by sulphur dioxide.

(c) The original colour of fabrics bleached by sulphur dioxide may sometimes be *restored*, on exposure to air, by the oxidising action of air and light, but *the bleaching action of chlorine is always permanent*.

(viii) When heated to 150° in a sealed tube, a solution of sulphurous acid deposits sulphur, **showing the presence of sulphur in sulphur dioxide :** $2H_2SO_3+SO_2 = 2H_2SO_4+S$.

(ix) Sulphur dioxide reacts with heated lead dioxide and sodium peroxide, yielding metallic sulphate :

$$PbO_2+SO_2 = PbSO_4 \text{ ; } Na_2O_2+SO_2 = Na_2SO_4.$$

(x) Sulphur dioxide reacts with oxygen in the presence of heated platinum, yielding sulphur-trioxide, and with chlorine in bright sunlight or in presence of charcoal, giving sulphuryl chloride.

$$2SO_2+O_2 \rightleftharpoons 2SO_3 \text{ ; } \quad SO_2+Cl_2=SO_2Cl_2$$

Tests.—(i) The gas is detected by its smell of burnt sulphur. (ii) A piece of paper soaked in acidified solution of potassium dichromate is turned green by sulphur dioxide. (iii) Any sulphite or bisulphite, on treatment with dilute hydrochloric or sulphuric acids, liberates sulphur dioxide, which may be recognised as above.

(iv) With barium chloride solution a sulphite solution gives a white precipitate of barium sulphite, soluble in hydrochloric acid ($BaSO_4$ is insoluble)—oxidising agents such as chlorine or bromine water precipitates barium sulphate from the solution : $BaSO_3 + H_2O + Br_2 = BaSO_4 + 2HBr$.

Uses.—(i) In the manufacture of sulphuric acid, in the refining of sugar and kerosene oil, and for bleaching delicate materials such as wool, silk and straw ; (ii) In the preparation of sodium and calcium bisulphites, both used for paper-making, and sodium metabisulphite, used in photography ; (iii) Sulphur dioxide has antiseptic properties and is used in fumigation and in preserving fruits ; (iv) Liquid sulphur dioxide is a refrigerant ; (v) The gas is also used as an *antichlor* in removing excess chlorine from bleached materials.

Absorbent.—An acidic oxide, SO_2 is absorbed by the alkalis, NaOH and KOH.

Sulphuric Acid, Oil of Vitriol, H_2SO_4.

Manufacture.—Sulphuric acid is made from sulphur dioxide by : (i) lead chamber process, and (ii) contact process.

The lead chamber process.—The principle of the chamber process involves the oxidation of moist sulphur dioxide by the oxygen of air in presence of oxides of nitrogen which act as a catalyst. An intermediate compound nitroso-sulphuric acid, $HO.SO_2.ONO$, is formed by the interaction of sulphur dioxide, oxygen, oxides of nitrogen and water ; the nitroso-sulphuric acid is readily decomposed by water into sulphuric acid and oxides of nitrogen, which react again :

$$2SO_2+N_2O_3+O_2+H_2O = 2HO.SO_2O.NO.$$

$$2HO.SO_2O.NO+H_2O=2HO.SO_2.OH+N_2O_3.$$

An alternative mechanism suggests that nitrogen dioxide oxidises sulphur dioxide to sulphur trioxide which with water yields sulphuric acid—the resulting nitric oxide is reoxidised by atmospheric oxygen to nitrogen dioxide, which reacts again :

$$SO_2 + NO_2 + H_2O = H_2SO_4 + NO \text{ ; } \quad 2NO + O_2 = 2NO_2.$$

The process is worked as follows. Sulphur dioxide is made by roasting iron pyrities, FeS_2, zinc blende, ZnS or elementary sulphur in a current of air in **burners B.**

$$4FeS_2+11O_2 = 2Fe_2O_3+8SO_2 \text{ ; } 2ZnS+3O_2 = 2ZnO+2SO_2.$$

The burner gases (fig. 60) containing about 8 per cent sulphur dioxide, 10 per cent oxygen and the rest nitrogen, pass through a **nitre-oven** N, where oxides of nitrogen are supplied by distilling a mixture of sodium nitrate and strong sulphuric acid from *nitre pots* and then through a **dust-catcher,** K, containing baffle-walls, where the suspended dust deposits.

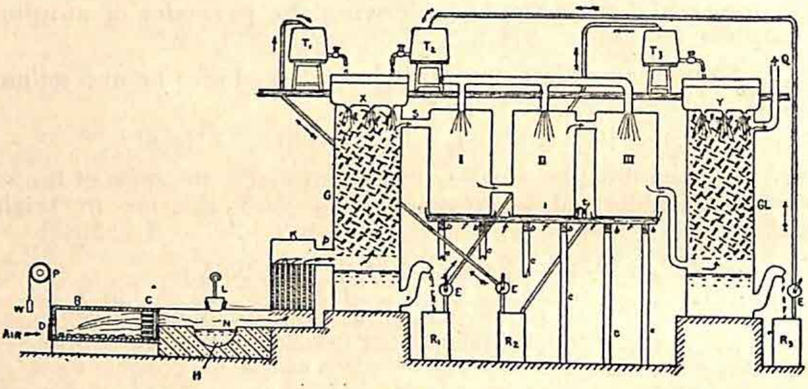


Fig. 60

In modern plants oxides of nitrogen are supplied by catalytic oxidation of ammonia.

From the dust-catcher the hot gases at about 300°-400° pass into the **Glover tower,** G—a lead tower lined with acid-resisting bricks and packed with flints down which are sprayed two streams of acid ; (i) the dilute chamber acid and (ii) the nitroso-sulphuric acid formed in the Gay-Lussac tower.

The Glover tower serves (i) to cool the burner gases to about 50° to 60° before entering the chambers, (ii) to concentrate the dilute chamber acid (65—70% acid) to about 78 per cent H_2SO_4 for sale or for use in the Gay-Lussac tower, (ii) to decompose the acid from the Gay-Lussac tower by the water in the dilute chamber acid so as to release the oxides of nitrogen which are returned to the chamber with the burner gases.

$$2HO.SO_2.O.NO + H_2O = 2HO.SO_2.OH + N_2O_3.$$

Besides, about 25 per cent of the total yield of the acid is formed in the tower. Hence the modern trend is to replace the chambers by a number of towers, called *reaction towers.*

The 78 per cent concentrated acid is collected at the base of the Glover tower.

From the Glover tower the gases enter, by a lead main, a set of **lead chambers,** I, II, and III made of sheet lead welded together by oxy-hydrogen flame. Water is sprayed from the top of the chambers and dilute (65 to 70 per cent) sulphuric acid, formed by the interaction of sulphur dioxide, oxygen, oxides of nitrogen and water, collects on the floor of the chambers whence it is withdrawn and pumped to top of the Glover tower for concentration. The strength of the chamber acid is kept at 65 to 70 per cent H_2SO_4 by regulated supply of water—still stronger acid attacks lead and also absorbs oxides of nitrogen, yielding nitroso-sulphuric acid, called **chamber crystals.** The chamber crystal may however be decomposed by admitting water in the chambers.

The gases from the last chamber, containing the valuable oxides of nitrogen, are led in the **Gay-Lussac tower,** Gl, a lead lined tower, packed with coke, down which flows a stream of 78 per cent sulphuric acid (from the base of the Glover tower) which absorbs the oxides of nitrogen as nitroso-sulphuric acid. The acid collected from the base of the Gay-Lussac tower is pumped to the Glover tower for denitration—the oxides of nitrogen are returned to the chambers, and the cycle of reactions is repeated. The waste gas from the Gay-Lussac tower passes to a chimney which maintains a draught through the plant.

Chamber acid contains about 65 to 70 per cent sulphuric acid. It is usually concentrated to 78% H_2SO_4 by passing through Glover tower. It may also be concentrated by evaporation in lead pans to 78% H_2SO_4 after which lead rapidly dissolves in the hot acid. The 78 per cent acid is known as **brown oil of vitriol or B.O.V.** Stronger acid, 95% H_2SO_4 is made by concentrating the B.O.V. in a current of hot air swept over its surface.

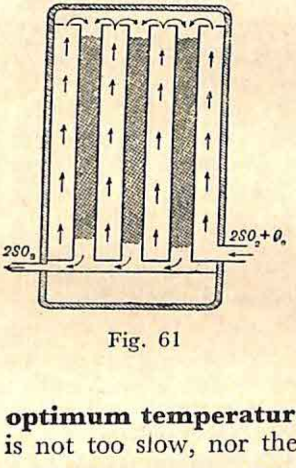


Fig. 61

The contact process.—The process consists in bringing about the combination of sulphur dioxide and oxygen (usually as air) to form sulphur trioxide by contact with a catalyst and the subsequent conversion of the sulphur trioxide into sulphuric acid.

(i) The formation of sulphur trioxide, as shown by the equation :

$2SO_2+O_2 \rightleftharpoons 2SO_3+45{,}000$ calories,

is an *exothermic* reversible reaction, and is therefore favoured at low temperature. But at low temperature the rate of formation of sulphur trioxide is too slow. Hence the reaction is carried out at an **optimum temperature** of 450°C such that the speed of the reaction is not too slow, nor the yield of sulphur trioxide too low.

The decomposition of trioxide becomes increasingly greater as the temperature rises. For a burner gas composition, 7 p.c. SO_2, 10 p.c. O_2 and 83 p.c. N_2 by volume, the percentages of SO_2 oxidised to SO_3 at different temperature are :

434° 99 ; 550° 85 ; 740° 60.

(ii) A catalyst such as *platinised asbestos*, *vanadium pentoxide*, *platinised silica gel*, is used to hasten the attainment of the equilibrium state at the comparatively low optimum temperature.

(iii) Excess of oxygen ensures complete conversion of sulphur dioxide to sulphur trioxide.

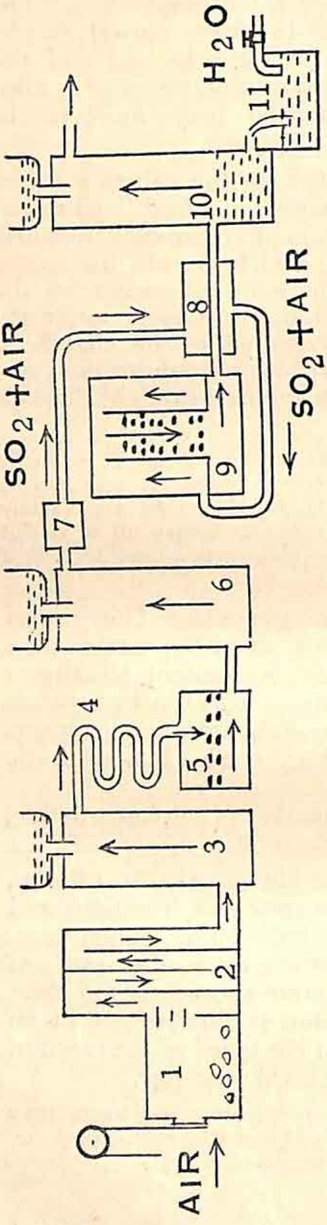


Fig. 62

(iv) The catalyst loses its activity due to '*poisoning*' by arsenious oxide, sulphuric acid mist, and dust, etc., which are present in the burner gases, and hence the necessity of removing these impurities from sulphur dioxide before it enters the contact chamber.

Sulphur dioxide is produced by by roasting iron pyrites or sulphur in a current of air in burners 1 (fig. 62). The gases from the *pyrites burner* (1) containing about 8% sulphur dioxide, 10% oxygen and the rest nitrogen, are carefully purified by passing in succession through :

(i) a *dust chamber* (2) where the gas is cleared of its dust and iron oxide cloud, (ii) a *lead tower* (3) meeting a flow of concentrated sulphuric acid, which removes the arsenious oxide and also cools the gas somewhat, (iii) water-cooled *lead coils* (4) where the gas is cooled to room temperature, (iv) *coke filters* (5) to remove chlorine (present as HCl) and to arrest acid mist, (v) a *drying tower* (6) packed with coke down which 93 p.c. sulphuric acid is flowing. The *purified and dry gas* must be *optically clear*, i.e., no fog is visible when a beam of light is sent through it in a chamber (7). The gases are finally fed via a *heat-interchanger* (8) (where they are preheated by the hot sulphur trioxide and nitrogen leaving the converter) into an iron cylinder, called a converter (9) (also fig. 61) fitted inside with vertical iron tubes packed with *platinised asbestos*. The incoming gases circulate round the hot tubes and then pass down them when sulphur dioxide is converted into sulphur trioxide. *The catalyst is kept at the optimum temperature of* 450°. Since the reaction is exothermic, no external heating is needed after once the reaction has been started.

The sulphur trioxide leaving the converter, *is absorbed in* 98 *per cent sulphuric acid* in the tower (10). $SO_3+H_2O = H_2SO_4$. Absorption of sulphur trioxide in water alone results in the formation of mist of droplets of acid. The strength of the absorption acid is kept at 98 per cent by regulated supply of water or dilute sulphuric acid.

If no water is added, sulphur trioxide dissolves in sulphuric acid, yielding **fuming sulphuric acid** or **oleum,** i.e., sulphuric acid containing dissolved SO_3.

Properties of sulphuric acid.—(i) Pure sulphuric acid is a heavy (density 1.838 at 15°), colourless, oily liquid which freezes at 10.4°. It decomposes at its boiling point, yielding dense white fumes of sulphur trioxide, $H_2SO_4 \rightleftharpoons SO_3+H_2O$ and forming a constant boiling mixture of 98.33 per cent sulphuric acid and water, boiling at 338°. 98 p.c. acid has a sp. gr. of 1.84.

(ii) Pure acid is a very poor electrical conductor but in aqueous solution it is a good conductor of heat and electricity.

(iii) It decomposes into sulphur dioxide, oxygen and water vapour when dropped on heated pumice stone.

$$2H_2SO_4 = 2H_2O+2SO_2+O_2.$$

(iv) **Affinity for water.**—Miscible with water in all proportions, concentrated sulphuric acid has great affinity for water. Much heat is evolved when the acid is mixed with water, forming the hydrates :

$$H_2SO_4, H_2O \; ; \; H_2SO_4, 2H_2O \; ; \text{ and } H_2SO_4, 4H_2O.$$

The great affinity of concentrated sulphuric acid for water is shown by its dehydrating action upon formic and oxalic acids, alcohol, sugar and starch—sugar and starch are charred by the acid with separation of carbon.

$C_{12}H_{22}O_{11}$ (sugar) $-11H_2O = 12C$; HCOOH (formic acid) $-H_2O = CO$.

Concentrated sulphuric acid is used for drying gases such as oxygen, nitrogen, sulphur dioxide and chlorine on which it does not act chemically.

(v) **Acid properties.**—In aqueous solution sulphuric acid behaves as a strong acid, since it is highly ionised. $H_2SO_4 \rightleftharpoons H^+ + HSO_4'$; $HSO_4' \rightleftharpoons H^+ + SO_4''$. Ionisation takes place in two stages. A dibasic acid it forms *acid* and *normal* salts, such as $NaHSO_4$ and Na_2SO_4.

Dilute sulphuric acid usually reacts with all metals (except lead) such as iron, magnesium, zinc, etc. standing *above* hydrogen in the electro-chemical series (p.110) liberating hydrogen and a salt of the metals but metals such as mercury, copper and silver standing *below* hydrogen in the series are not attacked by cold dilute sulphuric acid.

$$H_2SO_4 + Fe = H_2 + FeSO_4 \; ; \quad Mg + H_2SO_4 = H_2 + MgSO_4.$$

At the ordinary temperature it liberates carbon dioxide from carbonates and neutralises alkalis. At higher temperature sulphuric acid displaces the stronger nitric and hydrochloric acids from their salts, since it is less volatile than these acids :

$$NaCl+H_2SO_4 \rightleftharpoons NaHSO_4+HCl \; ; \; NaNO_3+H_2SO_4 \rightleftharpoons NaHSO_4+HNO_3.$$

(vi) **Oxidising properties.**—Hot concentrated sulphuric acid is an oxidising agent, and dissolves many metals such as zinc, lead, silver, mercury and copper, standing both *above* and *below* hydrogen in the electro-chemical series, yielding sulphur dioxide, water and a salt of the metal : $Pb+2H_2SO_4 = PbSO_4+2H_2O+SO_2$. Hot concentrated sulphuric acid oxidises sulphur to sulphur dioxide, carbon to carbon dioxide and phosphorus to phosphorous acid, H_3PO_3. It also decomposes HBr and HI, liberating bromine and iodine respectively.

$$S+2H_2SO_4 = 2H_2O+3SO_2 \; ; \; C+2H_2SO_4 = 2H_2O+CO_2+2SO_2;$$

$$2HBr+H_2SO_4 = 2H_2O+Br_2+SO_2; \; 3H_2SO_4+2P = 2H_3PO_3+3SO_2.$$

Tests.—Heated with copper turnings, concentrated sulphuric acid evolves sulphur dioxide, recognisable by the smell of burning sulphur. With barium chloride solution dilute sulphuric acid gives a white crystalline precipitate of barium sulphate, insoluble in concentrated hydrochloric acid.

$$BaCl_2 + H_2SO_4 = BaSO_4 + 2HCl.$$

A small quantity of a sulphate, $ZnSO_4$ for example, is fused on charcoal with sodium carbonate—the fused mass is then treated with dilute HCl and covered with a lead acetate paper which turns black. The reaction depends upon the formation of sulphide : $ZnSO_4 + 4C = ZnS + 4CO$. *This test detects sulphur in a sulphate.*

Uses.—Sulphuric acid is used in innumerable chemical industries—its consumption is indeed an index of industrial progress of a country. It is used (i) in the manufacture of hydrochloric and nitric acids, paints, pigments, dyes, glue and explosives, (ii) in the preparation of alum, fertilisers such as ammonium sulphate and superphosphate of lime, glucose from starch and (iii) in steel-pickling and galvanisation, in the refining of petroleum, in the parting of gold and silver, in textile industry, and in storage batteries. Oleum is used in sulphonation reactions in organic chemistry.

Exercises

1. Give a brief account of the allotropy of sulphur. How would you convert sulphur into (a) hydrogen sulphide, (b) sodium bisulphite, (c) ferrous sulphide and (d) sulphuric acid ?

2. How is hydrogen sulphide prepared and purified in the laboratory ? Describe the action of the gas on solution of : (a) ferric chloride, (b) lead nitrate, (c) sulphur dioxide, and (d) zinc sulphate. Explain why dilute sulphuric acid and not nitric acid is used for preparing hydrogen sulphide. Describe the reaction of the gas with (a) dilute nitric acid, (b) concentrated sulphuric acid, (c) iodine suspended in water.

3. Describe the preparation of pure and dry sulphur dioxide. What reactions take place when the gas is led into : (a) chlorine water, (b) caustic potash solution, (c) a mixture of nitrogen dioxide and water vapour, (d) cupric chloride, and (e) hydrogen sulphide ? State the uses of sulphur dioxide. *Calcutta* '59.

4. How is sulphuric acid manufactured by the lead chamber process ? State the principal uses of the acid. *Calcutta* '54.

5. Describe the manufacture of sulphuric acid by the contact process. Mention some important uses of the acid. *Calcutta* '54.

6. Describe experiments to show that sulphuric acid acts as (i) an acid, (ii) a dehydrating agent, (iii) an oxidising agent. Describe the action of the acid upon (a) sulphur, (b) lead, (c) potassium bromide, (d) common salt. Explain how you would distinguish between (i) a soluble sulphate and sulphide, (ii) chlorine and sulphur dioxide. *Calcutta* '53 ; 57.

XVI

PHOSPHORUS

Formula P_4; Atomic weight 30.98; Atomic number 15 ; B. Pt. 280.5°; M. Pt. 44.1° ; Density 1.83 yellow, 2.20 red.

Discovery.—In 1674-5 Brand, an alchemist of Humburg, who was seeking philosopher's stone, accidently discovered phosphorus by distilling evaporated urine—the phosphate, $Na(NH_4)HPO_4$, in the urine on heating forms the metaphosphate, $NaPO_3$, which is reduced to phosphorus by carbon separated from the charred organic matter.

$$4NaPO_3 + 5C = Na_4P_2O_7 + 5CO + 2P.$$

The element was called phosphorus, since it glows in the dark (*Phos = light ; phero* = I bear). In 1777 Scheele made phosphorus by distilling phosphoric acid with charcoal.

Occurrence.—Phosphorus occurs always in the combined state and mainly as phosphates. The chief minerals are : **fluorapatite,** $3Ca_3(PO_4)_2$, CaF_2, and **chlorapatite,** $3Ca_3(PO_4)_2$, $CaCl_2$—they are *hard* phosphates and are insoluble in dilute acids. Other phosphate minerals are **sombrerite** and **phosphorite,** $Ca_3(PO_4)_2$, **viviante,** $Fe_3(PO_4)_2$, $8H_2O$, and **wavelite,** $4AlPO_4$, $2Al(OH)_3$, $9H_2O$. **Coprolites** (calcium phosphate from fossil excreta) is a *soft-phosphate* and is soluble in dilute sulphuric acid.

As a normal constituent of plant and animal tissue, it is essential to their growth. It occurs especially in seeds, the yolk of eggs, the nerves and brain, and bone marrow, usually in the form of *lecithins* or glycero-phosphates. It is an essential constituent of bones in the form of calcium phosphate. Bones contain about 58 p.c. calcium phosphate plus some calcium carbonate, fat and nitrogenous organic matter. The fat may be extracted with carbon tetrachloride, and the organic matter dissolved out with hot water under pressure as *glue* or *gelatin*, and the residue then charred in closed retorts to form *animal charcoal* which is used in decolorising sugar. When no longer active, this is burnt to yield a residue, called **bone ash,** containing about 80 per cent calcium phosphate, with a little calcium carbonate and fluoride. *Bone ash is an important source of phosphorus.*

Preparation of phosphorus (i) In the old process bone ash or soft mineral phosphate was decomposed by hot and fairly strong (60 per cent) sulphuric acid, yielding phosphoric acid and insoluble calcium sulphate which was filtered off.

$$Ca_3(PO_4)_2 + 3H_2SO_4 = 3CaSO_4 + 2H_3PO_4.$$

The filtrate was concentrated to a syrup mixed with charcoal and dried until the phosphoric acid was converted to metaphosphoric acid HPO_3. The dried mass was distilled in fire clay retorts at bright-red heat—the vapour of phosphorus passing over was condensed under water.

$$H_3PO_4 = HPO_3 + H_2O \text{ ; } 4HPO_3 + 12C = P_4 + 2H_2 + 12CO.$$

This process has now been superseded by the electric furnace method.

(ii) **The electric furnace method.**—Phosphorus is now made by heating a phosphate mineral with sand and coke at a high temperature in an electric furnace by the *Readman, Parker and Robinson process.* A mixture of bone ash or mineral phosphate such as *apatite, sand and coke* is introduced through a hopper into a *closed electric furnace* made of brick work (fig. 63)—the charge being carried into the furnace by a screw conveyer. An electric arc is struck between carbon electrodes set towards the bottom of the furnace, to heat the charge. At the high temperature of the furnace, at about 1150°, silica displaces the more strongly acidic phosphorus pentoxide, owing to the volatility of the latter, forming calcium silicate. Phosphorus pentoxide is then reduced by the coke at about 1500°, to phosphorus vapour and carbon monoxide which leave the furnace by an exit at the top and bubbles through *water* under which phosphorus vapour condenses to yield *white phosphorus* and CO passes out. Fusible calcium silicate is run off at the bottom as a slag.

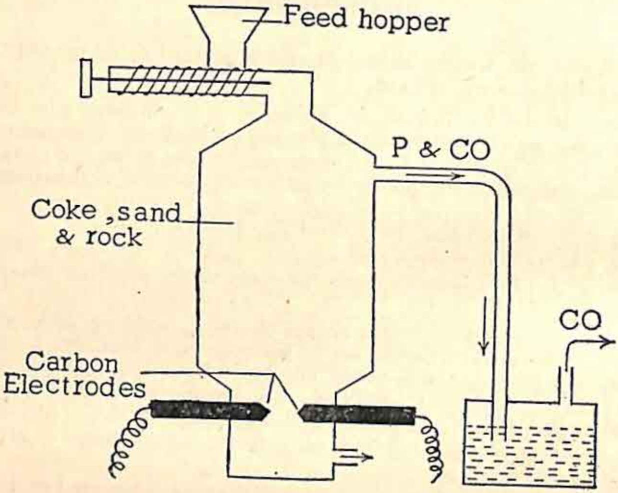


Fig. 63

$Ca_3(PO_4)_2+3SiO_2 = 3CaSiO_3+P_2O_5$; $2P_2O_5+10C = P_4+10CO$.

Crude phosphorus thus obtained is melted under hot water to separate it from sand, and stirred with a mixture of potassium dichromate and strong sulphuric acid ; some impurities are oxidised and pass into solution, and others separate and rise as a scum ; the liquid is filtered by pressing through chamois leather, cast into sticks by running into glass tubes cooled in water and finally packed with water in tin cans. *White phosphorus is stored and transported under water as it inflames in air.*

Properties of phosphorus.—(i) White (or yellow) phosphorus is a translucent soft, waxy, white, crystalline, low-melting solid, very sparingly soluble in water (1 in 300,000) but, *readily soluble in carbon disulphide*, ether, olive oil, benzene and alcohol. It is a non-conductor of heat and electricity. *It is highly poisonous*—the lethal dose being about 0.15 gm. Its vapour density corresponds with P_4.

(ii) It ignites in air at the low temperature of 35°, yielding phosphorus pentoxide, and hence *phosphorus is always kept and handled under water*. $4P+5O_2 = 2P_2O_5$.

Exposed to air at the ordinary temperature white phosphorus undergoes spontaneous oxidation, yielding white fumes of a lower oxide and some ozone and emitting a *green glow or* **phosphorescence,** visible in the dark.

Even a trace of phosphorus (1 in 500,000) gives this glow and its formation is used to detect phosphorus in cases of phosphorus poisoning.

Expt. 1.—On carefully adding concentrated sulphuric acid to a mixture of pieces of white phosphorus and potassium chlorate kept under water in a jar, phosphorus ignites under water, giving sparks of fire under water.

Expt. 2.—Cold flame experiment.—Few pieces of dry white phosphorus are placed in a flask and covered with dry glass wool—the flask is fitted with a cork and two tubes. The flask is heated on a water-bath and a stream of carbon dioxide is passed through. The phosphorus vapour carried along with the gas oxidises in the air and a *green flame* of glowing phosphorus is produced at the mouth of the exit tube. The flame is quite cold to the hand and does not kindle a match.

The phosphorescent light of fireflies is due to the oxidation of a substance known as *luciferin* by the enzyme *luciferase.*

(iii) It inflames spontaneously in halogens, yielding halides of phosphorus :

$$P_4+6Cl_2 = 4PCl_3\ ;\ P_4+10Cl_2 = 4PCl_5\ ;\ P_4+6I_2 = 4PI_3.$$

(iv) It dissolves in hot caustic alkali, yielding phosphine and hypophosphite : $P_4+3NaOH+3H_2O = PH_3+3NaH_2PO_2$.

(v) It is oxdised to phosphoric acid by hot concentrated nitric acid. $P_4+10HNO_3+H_2O = 4H_3PO_4+5NO+5NO_2$.

White phosphorus must never be touched with the fingers. It is cut *under water* with a knife using tongs.

(iv) White phosphorus reacts with cold copper sulphate, giving metallic copper ; white phosphorus, if accidentally dropped on the hand, may be removed by washing with copper sulphate solution :

$$2P + 5CuSO_4 + 8H_2O = 5Cu + 2H_3PO_4 + 5H_2SO_4.$$

Colloidal solution of gold is obtained by reducing auric chloride solution with phosphorus dissolved in ether.

In cases of phosphorus poisoning copper sulphate is administered as an emetic, followed by hydrogen peroxide.

Allotropy of phosphorus.—Two main allotropes of phosphorus are : (a) *white* (or *yellow*) *prosphorus*, (b) *red phosphorus.* White phosphorus, metastable at the ordinary temperature and is slowly transformed into the stable red variety with evolution of heat.

White P = red P + 4220 calories.

Red phosphorus.—Red phosphorus is obtained by subjecting white phosphorus to *silent electric discharges* or by heating it at 250° in an atmosphere of nitrogen or carbon dioxide in presence of a trace of iodine as a catalyst.

Red phosphorus is obtained by heating white phosphorus in a cast iron pot fitted with an air-tight cover through which passes an upright tube, open at both ends, so that the pressure inside the pot does not exceed one atmosphere. The temperature is kept at 240°. A portion of phosphorus is oxidised by the oxygen of air in the pot, and the rest is slowly transformed into solid red phosphorus. The red phosphorus thus obtained is cooled, ground under water, boiled with caustic soda solution to remove any unchanged white phosphorus, and filtered. It is then washed with hot water and dried with steam.

Conversion of red phosphorus to yellow phosphorus.—A little red phosphorus is placed in a hard glass test tube, fitted with a rubber stopper and two tubes. The air within the test tube is displaced by a current of carbon dioxide. The red phosphorus is then heated in a slow current of carbon dioxide when white phosphorus condenses on the upper cooler part of the test tube.

Comparison of white and red phosphorus.—White phosphorus is unstable ; it slowly passes into red phosphorus which is stable. White phosphorus is more reactive chemically than red phosphorus. They differ greatly in their physical and chemical properties as shown in the table :

Property	White phosphorus	Red phosphorus
(i) Colour	Colourless or pale yellow	Reddish-violet
(ii) Smell	Garlic smell	Odourless
(iii) Specific gravity	1.83	2.20
(iv) Melting point	44.1°	592.5° under pressure
(v) Boiling point	280.5°	Very high
(vi) Ignition temp. in air	35°C	260°C
(vii) Solubility in water	Very sparingly soluble	Insoluble
(viii) Solubility in CS_2	Soluble	Insoluble
(ix) Action of air	Spontaneous oxidation with green glow or phosphorescence	Does not glow, i.e., no phosphoresence ;
(x) Action of chlorine	Ignites spontaneously	Ignites on heating.
(xi) Hot caustic alkali	Dissolves evolving PH_3	No action
(xii) Chemical activity	Very reactive	Less active than white P
(xiii) Electrical conductivity	Non-conductor	Feeble conductor
(xiv) Stability	Metastable allotrope	Stable allotrope
(xv) Physiological action	Intensely poinsonous	Non-poisonous.

Uses of Phosphorus.—(i) In the manufacture of matches—yellow phosphorus in lucifer matches, and red phosphorus in safety matches, (ii) In the preparation of phosphorus pentoxide, phosphor bronze, hypophosphite of lime, and red phosphorus, (iii) In making tracer bullets, incendiary bombs, and in producing smoke screen, and (iv) As a poison for rats.

Phosphorus tri- and penta-chlorides.—Phosphorus trichloride, PCl_3, a liquid, is made by passing *dry* chlorine over white phosphorus. It is hydrolysed by water, giving phosphorus acid.

$$2P + 3Cl_2 = 2PCl_3 \; ; \quad PCl_3 + 3H_2O = H_3PO_3 + 3HCl$$

Phosphorus pentachloride, PCl_5, white powder, is made by burning phosphorus in excess of chlorine or by the action of chlorine on cold phosphorus trichloride.

$$2P + 5Cl_2 = 2PCl_5 \; ; \quad PCl_3 + Cl_2 \leftrightharpoons PCl_5$$

PCl_5 dissociates by heat to chlorine and PCl_3. PCl_5 is hydrolysed by water, giving phosphorus oxychloride and finally phosphoric acid.

$$PCl_5 + H_2O = POCl_3 + 2HCl$$

$$POCl_3 + 3H_2O = H_3PO_4 + 3HCl$$

Oxides and oxyacids of phosphorus.—The principal oxides and oxyacids of phosphorus are :

—	Hyphosphorous acid H_3PO_2
Phosphorus trioxide P_2O_3	Phosphorous acid H_3PO_3
Phosphorus pentoxide P_2O_5	Orthophosphoric acid H_3PO_4
	Pyrophosphoric acid $H_4P_2O_7$
	Metaphosphoric acid HPO_3

Phosphorus pentoxide, P_2O_5, is prepared by igniting phosphorus in excess of dry air or oxygen. $P_4 + 5O_2 = 2P_2O_5$.

It is a white deliquescent powder which sublimes at 250° ; its vapour density corresponds to the formula P_4O_{10}. *An acidic oxide,* it dissolves in *cold* water, giving metaphosphoric acid ; with *boiling* water orthophosphoric acid is produced :

$$P_2O_5 + H_2O = 2HPO_3 \; ; \; P_2O_5 + 3H_2O = 2H_3PO_4.$$

It has great affinity for water, and is the *most effective drying agent ;*

thus it dehydrates sulphuric and nitric acids, yielding their anhydrides :

$$H_2SO_4+P_2O_5 = 2HPO_3+SO_3\ ;\ 2HNO_3+P_2O_5 = 2HPO_3+N_2O_5.$$

The phosphoric acids.—Three phosphoric acids are formed by the addition of water to prosphorus pentoxide, which, therefore, is the anhydride of the three acids :

$$P_2O_5 + H_2O = 2HPO_3 \text{ (meta-phosphoric acid) ;}$$
$$P_2O_5 + 2H_2O = H_4P_2O_7 \text{ (pyro-phosphoric acid) ;}$$
$$P_2O_5 + 3H_2O = 2H_3PO_4 \text{ (ortho-phosphoric acid).}$$

When heated to 213°, the ortho-phosphoric acid is slowly transformed into pyrophosphoric acid, which in its turn is converted into a glassy mass of meta-phosphoric acid, when heated to 316°. Heated still further the meta-phosphoric acid also dehydrates on prolonged heating, yielding some phosphorus pentoxide. The changes are reversible :

$$2H_3PO_4 \underset{+H_2O}{\overset{-H_2O}{\rightleftharpoons}} H_4P_2O_7 \underset{+H_2O}{\overset{-H_2O}{\rightleftharpoons}} 2HPO_3 \underset{+H_2O}{\overset{-H_2O}{\rightleftharpoons}} P_2O_5.$$

Ortho-phosphoric acid, H_3PO_4.—Common phosphoric acid is orthophosphoric acid. It is made : (a) by digesting bone ash with dilute (60%) sulphuric acid in a lead-lined tank for several hours—the mixture is heated by open steam. The bone ash is decomposed by the sulphuric acid, yielding phosphoric acid and calcium sulphate. The insoluble calcium sulphate is filtered off on a bed of coke, and the phosphoric acid solution is evaporated to a thick syrupy liquid of sp. gr. 1.7, containing 85% phosphoric acid. $Ca_3(PO_4)_2+3H_2SO_4 = 3CaSO_4+2H_3PO_4$.

(b) by heating a phosphate mineral with coke and silica in an electric furnace, the resulting phosphorus vapour and CO (*vide* preparation of phosphorus) are burnt to P_2O_5 and CO_2 by admiting air. Water is sprayed in the cooled gases when 85 per cent phosphoric acid is obtained—any mist of phophoric acid formed is separated by electrostatic precipitation. $P_2O_5+3H_2O = 2H_3PO_4$.

Pure phosphoric acid is obtained by boiling red phosphorus with concentrated nitric acid in a flask fitted with a reflux condenser on a waterbath. A crystal of iodine catalyses the reaction. The resulting solution is concentrated till the temperature rises just to 180°, and then cooled in a vacuum desiccator over concentrated sulphuric acid—the desiccator being placed in a freezing mixture—when colourless crystals of phosphoric acid, m. pt. 42°, deposit.

$$P_4 + 10HNO_3 + H_2O = 4H_3PO_4 + 5NO + 5NO_2.$$

The phosphates.—Phosphoric acid is *tribasic* and forms three series of salts such as *primary phosphate*, NaH_2PO_4 (monosodium dihydrogen phosphate), *secondary phosphate*, Na_2HPO_4 (disodium monohydrogen phosphate), and tertiary phosphate, Na_3PO_4 (trisodium phosphate).

The three hydrogen ions dissociate in stages from phosphoric acid, the first one readily, the second with difficulty and third in presence of excess alkali only.

$$H_3PO_4 \rightleftharpoons H^+ + H_2PO_4' \rightleftharpoons 2H^+ + HPO_4'' \rightleftharpoons 3H^+ + PO_4'''$$

The primary phosphate is *acid* to litmus :

$$NaH_2PO_4 \rightleftharpoons Na^+ + H_2PO_4'\ ;\ H_2PO_4' \rightleftharpoons H^+ + HPO_4''.$$

The secondary phosphate is *faintly alkaline* (practically neutral), the tertiary phosphate *strongly alkaline*, since they are hydrolysed by water :

$$Na_2HPO_4 + H_2O \leftrightharpoons NaH_2PO_4 + NaOH$$

$$Na_3PO_4 + H_2O \leftrightharpoons Na_2HPO_4 + NaOH.$$

The primary and secondary phosphates decompose on heating with elimination of water :

(i) a primary phosphate yields a metaphosphate :

$NaH_2PO_4 = H_2O + NaPO_3$ (sodium metaphosphate)

(ii) a secondary phosphate yields a pyrophosphate :

$2Na_2HPO_4 = H_2O + Na_4P_2O_7$ (sodium pyrophosphate)

(iii) a tertiary phosphate remains unchanged by heat.

Phosphates containing ammonium radicals, lose both water and ammonia on heating : $(NH_4)_2HPO_4 = HPO_3 + H_2O + 2NH_3$;

$$2MgNH_4PO_4 = Mg_2P_2O_7 + H_2O + 2NH_3$$

$Na(NH_4)HPO_4$ (microcosmic salt) $= NaPO_3 + H_2O + NH_3$.

Phosphate	Effect of heat	Phenolphthalein	Methyl orange
(i) Primary NaH_2PO_4	decomposes ; forms metaphosphate	acid	neutral
(ii) Secondary Na_2HPO_4	decomposes ; forms pyrophosphate	neutral	alkaline
(iii) Tertiary Na_3PO_4	does not decompose	alkaline	alkaline

Test for phosphate.—(i) *Cobalt nitrate test.*—Heated on charcoal with a drop or two of cobalt nitrate solution in the oxidising flame a phosphate yields *a blue mass.*

(ii) *Ammonium molybdate test.*—On adding few drops of a orthophosphate solution to an excess of ammonium molybadte acidified with concentrated nitric acid a *canary-yellow* precipitate of ammonium phosphomolybdate slowly deposits in the cold and rapidly at 60°—65°. Arsenates also respond to this test but *only on boiling.*

(iii) Silver nitrate solution gives a yellow precipitate with a solution of an orthophosphate.

Phosphorus trioxide, P_2O_3, is formed by burning phosphorus in a limited supply of air : $P_4 + 3O_2 = 2P_2O_3$.

Phosphorus trioxide is a white crystalline solid, m.p. 23.8°, and b. p. 175°. Its vapour density shows the formula to be P_4O_6. It dissolves in cold water, forming phosphorus acid of which it is the anhydride ; with hot water it gives phosphine and phosphoric acid :

$$P_2O_3 + 3H_2O = 2H_3PO_3 : 2P_2O_3 + 6H_2O = PH_3 + 3H_3PO_4.$$

Exercises

(1) Describe the preparation of white phosphorus. How is it converted to red phosphorus ? Compare the properties of these two forms of phosphorus. What happens when (a) each form of phosphorus is boiled with caustic soda solution, (b) red phosphorus is heated with concentrated nitric acid, and (c) slow stream of chlorine is passed through white phosphorus melted under water ? State the main uses of phosphorus. *Calcutta* '57.

(2) Starting from bone ash how you will prepare (a) phosphorus, (b) phosphoric acid. State their chief properties and uses.

(3) Give in outline the preparation of chief oxides and the chlorides of phosphorus. State the action of water on each of them.

XVII

CARBON AND ITS COMPOUNDS

Symbol of carbon C ; atomic weight 12.010 ; atomic number 6.

Occurrence.—Elementary carbon occurs in nature as *diamond* and *graphite.* It is present in air as carbon dioxide (about 3 volumes in 10,000) and as carbonate in sedimentary rocks such as *limestone* and *dolomite*. An essential constituent of all animal and vegetable bodies, it is found as *carbohydrates* such as starch, sugar and cellulose, all occurring in plants, and as *proteins*, such as albumin and gelatin, occurring both in plants and animals. It is present in petroleum as *hydrocarbons*. Coal is a carbonaceous mineral of vegetable origin.

The Allotropy of carbon.—The different crystalline and amorphous allotropic forms of carbon are :

(i) *crystalline : diamond* and *graphite ;*
(ii) *amorphous : charcoal, lampblack* (or *soot*), *coke, gas carbon.*

Graphite is the stablest form of carbon. The amorphous carbon has been shown by X-ray analysis to be micro-crystalline graphite in structure.

The identity of the allotropic forms of carbon, such as diamond, graphite and charcoal, is established by burning equal weights of the three varieties in a current of pure and dry oxygen and absorbing the carbon dioxide formed in previously weighed tubes containing caustic potash when equal weights of the same product carbon dioxide are obtained. $C+O_2 = CO_2$.

About 0.5 g. of an allotrope of carbon is weighed out in a porcelain boat which is then placed in a hard-glass tube C (fig. 64). The carbon is gently heated in a current of pure and dry oxygen (which is bubbled through strong sulphuric acid in A and thereby dried), and the carbon dioxide formed absorbed in the previously weighed potash tubes B.

The identity of different allotropes of sulphur may be similarly established.

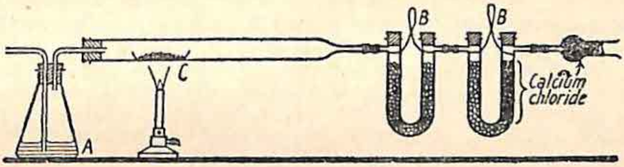


Fig. 64

Diamond.—It occurs naturally in Golconda in India, South Africa, Brazil, the Ural mountain and elsewhere. South African mines alone supply over 96% of the world's diamonds. Indian diamond occurs in river gravels and alluvial deposits, and are separated by washing.

Diamonds are rated in *carats*—one *carat* = 0.2054 gm. The world famous gem *Kohinoor* originally weighed 186 carats, but had to be cut to 106 carats.

Properties.—(i) Diamond forms transparent lustrous crystals of high refractive index 2.42, for light—colourless diamonds are almost pure carbon. Transparent diamonds are occasionally pink, green or blue.

(ii) It is the densest form of carbon with a specific gravity 3.52 and is a non-conductor of heat and electricity. It is transparent to X-rays—the imitation diamond (made of glass) is opaque to the rays.

(iii) Diamond is extremely hard and is not scratched by any substance (except boron carbide B_4C).

(iv) Very inert chemically, it is not attacked by acids, alkalis or fused potassium chlorate.

Uses of diamond.—Diamonds are generally cut for gems and also used, on account of their extreme hardness, for cutting glass and for rock-boring purposes. The opaque and black diamonds known as *carbonado* and *bort*, being less valuable, *are usually used for rock-drilling, and also for cutting and polishing diamonds and stones. Diamonds can be cut only by other diamonds.*

Graphite.—Graphite (*grapho*, I write), also called **plumbago** or **black lead,** is found in Ceylon, Siberia, Bohemia, California and elsewhere.

Properties.—(i) Unlike diamond, graphite is opaque, *soft* and greasy to the touch with an almost *metallic lustre* and *conducts heat and electricity;* it is also less dense—its specific gravity is 2.25.

(ii) Like diamond, graphite is crystalline—their crystalline forms are different, graphite having hexagonal and diamond tetrahedral arrangement of the carbon atoms in the crystals. Grey, flaky hexagonal crystals of graphite *easily mark paper*, and hence the use of graphite in the so-called *lead-pencils.*

(iii) Slightly more reactive than diamond, graphite is oxidised to CO_2 in air at 700°, and to CF_4 in fluorine at 500°. Though unattacked by dilute acids, caustic alkalis or chlorine, it is slowly oxidised to CO_2 by chromic acid, and to CO by fused sodium carbonate.

(iv) Unlike diamond, it is oxidised below 100° to a yellow insoluble solid, *graphitic acid.* $C_{11}H_4O_5$ by a mixture of concentrated sulphuric and nitric acids and potassium chlorate. *Formation of graphitic acid is regarded as a test for graphite.*

Uses of graphite.—(*i*) Graphite is used in making so-called *lead pencils*, and for *polishing iron stoves*, (*ii*) Colloidal graphite as a suspension in oil is used in *lubricating* machinery, (*iii*) Since it conducts electricity, it is used in making electrodes and *heating elements* in electric furnaces, and for coating articles of non-conducting materials meant for *electro-typing*, (*iv*) Mixed with clay, it is used in making *plumbago crucibles* which combine refractory properties with thermal conductivity.

Amorphous carbon.—**Charcoals :** There are different varieties of charcoal, depending upon the source, such as wood charcoal, sugar charcoal, and animal charcoal.

(i) **Wood charcoal.**—This is made by the dry distillation of wood in externally heated iron retorts (fig. 65) from which air is excluded. The products of distillation are (a) the inflammable gas, known as *wood gas*, used for heating the retorts, (b) the volatile liquid distillate, consisting of *wood tar* and an aqueous portion, called *pyroligneous acid* which contains acetic acid,

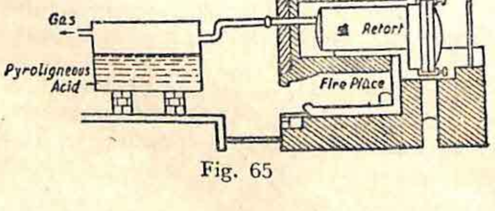


Fig. 65

methyl alcohol and acetone, and (c) the solid residue of *wood charcoal* in the retort. Average yield : wood charcoal 25%, wood gas 25% pyroligneous acid 40%, and wood tar 10%.

Wood tar finds use as a *fuel ;* on refining it gives *wood oil* (a solvent), *creosote oil* (wood preservative), *guaiacol* (a medicinal product) and *pitch.*

There is a wood distillation plant at Bhadrabati in the Mysore State.

(ii) **Sugar charcoal.**—This is obtained by heating pure cane sugar in a covered vessel till no more gas is evolved—the resulting charcoal is then heated to 1000°C in a graphite tube in a current of chlorine to remove the residual combined hydrogen as hydrogen chloride. It is next washed with water and dried in a current of hydrogen to remove chlorine. *Sugar charcoal is the purest form of carbon.*

It may also be obtained by the action of strong sulphuric acid upon a concentrated cane sugar solution—charcoal separating as a black mass is washed with water, filtered and dired.

$$C_{12}H_{22}O_{11} \text{ (cane sugar)} = 12C + 11H_2O.$$

(iii) **Animal Charcoal (bone charcoal or bone black).**—This is made by the destructive distillation of bones in closed retorts—the volatile products distilling over condense into : (a) an alkaline watery liquid containing ammonia and nitrogenous organic bases, and (b) *bone oil* or *Dippel's oil* containing pyridine, etc. The black residue in the retort containing about 10 percent carbon deposited on a porous framework of 90% calcium phosphate and calcium carbonate, etc., is known as *animal charcoal.* The charcoal that remains after dissolving out the calcium salts with hydrochloric acid is known as **ivory black.**

Blood on charring by similar treatment yields *blood charcoal.*

Cocoanut shells on being heated in absence of air yields an active form of charcoal. **Activated charcoal** is obtained by carbonising wood previously impregnated with zinc or magnesium chloride. It may also be made by heating wood charcoal prepared at 850°—900° in a current of steam, when the material (inactive graphite layer on the surface) obstructing the pores is removed.

Properties of charcoal.—(i) Bad conductor of heat and electricity, charcoal is black, soft and highly *porous* substance of varying sp. gr. of about 1.4 to 1.9 ; but its density is reduced to about 0.2 by air enclosed in its pores, and hence *charcoal floats on water.*

(ii) Because of its porosity, it readily adsorbs gases—the adsorbed gases are released on heating. Charcoal may also adsorb dissolved substances from a solution.

Experiments.—(a) A piece of red-hot wood-charcoal is inserted into a tube of ammonia standing over mercury—mercury rises up the jar as the charcoal absorbs the gas ; the charcoal takes up about 90 times its volume of ammonia gas—the activated charcoal absorbs a much larger volume.

(b) A hot solution of a sample of crude sugar, brown in colour, is shaken with animal charcoal and then filtered—the filtrate is the colourless solution of sugar—the colouring matter adsorbed and retained by the charcoal.

(c) A dilute solution of litmus is boiled with animal charcoal and filtered—the filtrate runs through colourless ; the litmus is being adsorbed by the charcoal.

Similar experiment may be done with indigo solution. Activated charcoal is a better adsorbent than ordinary charcoal.

(iii) Insoluble in water, alkalis and non-oxidising acids, charcoal is resistant to the action of chlorine, bromine, and iodine ; but unlike diamond and graphite it is oxidised to CO_2 by hot conc. H_2SO_4 a small amount of mellitic acid is produced at the same time. It is also oxidised by hot conc. HNO_3.

$$C+2H_2SO_4=CO_2+2SO_2+2H_2O;C+4HNO_3=CO_2+4NO_2+2H_2O$$

(iv) Charcoal ignites in oxygen a little above 400°C, whereas graphite burns at 700° and diamnnd at 800°. It ignites spontaneously in fluorine, yielding CF_4, while graphite burns at 500° and diamond at 700°.

(v) *Charcoal is a good reducing agent at high temperatures.* It reduces many metallic oxides such as CuO, PbO, Fe_2O_3, ZnO and SnO_2 to the respective metals ; thus copper oxide is reduced to red mass of metallic copper on being heated with charcoal powder. Red hot charcoal reduces steam to hydrogen, and carbon dioxide to carbon monoxide.

$$CuO+C = Cu+CO \; ; H_2O+C = H_2+CO \; ; CO_2+C = 2CO.$$

(vi) Carbon combines with hydrogen at high temperature and pressure yielding methane in very small amounts ; acetylene is formed if a spark is passed between carbon electrodes in hydrogen. Carbon combines with sulphur vapour, giving carbon disulphide. $C + 2S = CS_2$; $2C + H_2 = C_2H_2$.

Uses of charcoal.—(*i*) Wood charcoal is used as a fuel and as a reducing agent, in making filter-beds and gun-powder. It is very often used in sewers and hospitals to remove obnoxious gases by adsorption.

(*ii*) Animal charcoal is extensively used in the refining of sugar ; ivory black is used as a pigment.

(*iii*) Activated charcoal is used in making gas-masks.

Lamp black.—It is a fine variety of soot, prepared by burning substances rich in carbon such as kerosene, tar, turpentine and rosin, in a limited supply of air, and collecting the soot by deposition on cold surfaces—the smoke is conveyed into a chamber where it is deposited on wet suspended blankets and is subsequently removed. A fine variety, known as *gas black*, is prepared from natural gas which is methane mainly. It is a bad conductor of heat and electricity.

It is used in making printer's ink, black paint and boot-polish and in vulcanizing rubber. Lamp black contains some oily impurities which can be removed by heating in chlorine.

Coal.—Coal is a carbonaceous mineral of vegetable origin. It is the final result of a series of slow decompositions of vegetable matter of very remote past, in presence of a limited supply of air and under high pressure due to the weight of superimposed strata, in the womb of the earth. Various stages of decomposition are represented by :

Peat, lignite or brown coal, bituminous coal and anthracite.

Coke and gas carbon.—They are the by-products of coal gas industry. Very hard and compact, coke is used as a reducing agent in metallurgy. It is also used as a fuel. Coke is a bad conductor of heat and electricity.

Gas carbon is obtained as a hard deposit on the hot walls of the retorts by the thermal decomposition of hydrocarbons during the manufacture of coal gas. A good conductor of heat and electricity, it is used in making *electrodes* for arc-lights and electric *batteries*, and brushes for motors and dynamos.

Properties of different forms of carbon

Property	Diamond	Graphite	Amorphous carbon
1. Colour and appearance etc.	Colourless transparent crystals, high refractive index and brilliant lustre.	Greyish-black crystals, metallic lustre, marks paper.	Black amorphous
2. Specific gravity.	3.5	2.25	Charcoal 1.4 to 1.9; gas carbon 2.35.
3. Hardness ; porosity.	Extremely hard but fairly brittle.	Extremely soft, greasy to touch, marks paper.	Charcoal : soft and porous ; soot : light, hard and soft ; gas carbon : hard ; soft bituminous coal and hard anthracite.
4. Electrical conductivity.	Bad conductor.	Good conductor.	Bad conductor except gas carbon which is a good conductor.
5. Adsorbing power of gas etc.	—	—	Charcoal alone is a decoloriser, deodoriser ; adsorbs gases.
5. Effect of heat.	Forms graphite at 1800°.	Stable form at high temperature.	Changes to graphite at high temperature
7. Burns with flame in oxygen.	CO_2 at 800°—850°; high ignition temperature.	CO_2 at 690°C.	CO_2 at 345°C (wood charcoal) ; low ignition temperature.
8. Reacts with fluorine.	CF_4 at 700°C.	CF_4 at 500°C.	Ignites spontaneously to CF_4.

Oxides of Carbon.—Carbon forms two important oxides namely carbon monoxide, CO, and carbon dioxide, CO_2, which are both gaseous.

Carbon dioxide CO_2

Critical temperature 31°C. Critical pressure 72.8 atm. Boiling point—56°C at 5.3 atm. Sublimes at —78.52°C. Solubility at 0°C 1.7 vol. in 1 vol. water.

History and occurrence.—The gas, called *gas sylvestre* by Van Helmont who discovered it in 1630, was studied by Black (1754) who gave it the name *fixed air*. But it was Lavoisier who showed it to be an oxide of carbon in 1783.

In the free state it occurs in air to the extent of 0.03% by volume. The carbon dioxide of the air is mainly produced by the combustion of fuels, decay of organic matter and respiration of animals. Fermentation of sugar also produces the gas.

In combination it occurs as carbonates, such as chalk, limestone, magnesite, dolomite, etc.

Preparation.—Carbon dioxide is formed (i) by the direct combustion of carbon in excess of air or oxygen, (ii) by the action of dilute acid on all metallic carbonates or bi-carbonates :

$$Na_2CO_3+H_2SO_4 = Na_2SO_4+H_2O+CO_2; \quad NaHCO_3+HCl = NaCl+H_2O+CO_2.$$

(iii) By heating all metallic carbonates (except those of alkali metals and barium) or bi-carbonates.

$$CaCO_3 = CaO + CO_2 \; ; \quad Ca(HCO_3)_2 = CaCO_3 + H_2O + CO_2.$$

(iv) By heating sodium or potassium bicarbonates.

$$2NaHCO_3 = Na_2CO_3 + H_2O + CO_2.$$

Laboratory preparation.—Carbon dioxide is usually prepared by the action of acids upon carbonates. The gas is obtained in the laboratory by the action of cold dilute hydrochloric acid upon marble (calcium carbonate) :

$$CaCO_3+2HCl = CaCl_2+H_2O+CO_2.$$

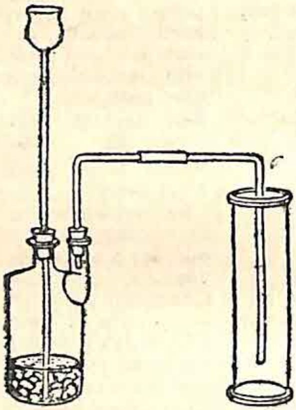


Fig. 66

Some marble chips are taken in a Woulfe's bottle (fig. 66) fitted with a thistle funnel and a delivery tube, and covered with water. On pouring moderately strong hydrochloric acid, quick effervescence takes place due to the evolution of the carbon dioxide—the gas may be collected over water (though it is somewhat soluble) or by the upward displacement of air, since it is $1\frac{1}{2}$ times heavier than air. The gas may be washed with water (to remove HCl vapour), dried by sulphuric acid or calcium chloride and collected over mercury.

Kipp's apparatus is charged with marble and hydrochloric acd for a ready supply of the gas.

Dilute sulphuric acid cannot be used with marble, since the sparingly soluble calcium sulphate produced covers the marble and soon stops the action of the acid.

Pure carbon dioxide is best obtained heating pure sodium bicarbonate : $2NaHCO_3 \leftrightharpoons Na_2CO_3+H_2O+CO_2$.

Properties.—(i) Carbon dioxide is a colourless gas with a faint pungent smell and an acid taste, easily liquefiable under pressure —at temperatures below 31°, its critical point, it may be compressed to a liquid.

(ii) The gas is not poisonous but it does not support respiration, since animals feel suffocated in its atmosphere for want of oxygen.

(iii) The gas is about $1\frac{1}{2}$ times heavier than air.

The gas is poured from one jar to another just as water is poured—on adding lime water to the lower jar, it turns milky, showing that the gas is heavier than air. A soap bubble (containing air) floats on the surface of the heavier gas carbon dioxide.

(iv) It is fairly soluble in water—water dissolving its own volume of the gas at 15° ; the gas is completely expelled on boiling the solution. The solution is acidic due to the formation of *unstable carbonic acid, known only in solution.* The solubility of the gas increases under pressure.

$$H_2O + CO_2 \leftrightharpoons H_2CO_3.$$

Carbon dioxide is passed into blue litmus solution—it turns dull red. The blue colour is restored on boiling—carbon dioxide being removed. Hence the solution of the gas is a weak unstable acid.

(v) The gas does neither burn nor supports combustion, and hence its use as a fire extinguisher. *But ignited Na, K and Mg burn in the gas with separation of carbon.*

$$4K+3CO_2 = 2K_2CO_3+C\ ; \quad CO_2+2Mg = C+2MgO.$$

A piece of burning magnesium is inserted into a jar of carbon dioxide, it continues burning with separation of soot ; when shaken with dilute HCl, magnesium oxide dissolves, black particles of carbon are seen floating in the liquid. The experiment shows the presence of carbon in carbon dioxide.

(vi) The gas may be reduced to carbon monoxide, passing over red hot carbon, iron or zinc :

$$CO_2+C = 2CO\ ; \qquad CO_2+Fe = CO+FeO.$$

(vii) An acidic oxide, the gas reacts with bases and alkalis, yielding carbonates : $CaO+CO_2 \leftrightharpoons CaCO_3$; $Na_2O+CO_2 = Na_2CO_3$.

Expt.—(a) **Action on lime water :**—Carbon dioxide is passed into lime water; it turns milky due to the formation of white insoluble calcium carbonate. The milkiness disappears on continued passing of the gas owing to the formation of soluble calcium bicarbonate. The milkiness appears on boiling the solution, since the bicarbonate decomposes, yielding the carbonate back.

$$CO_2 + Ca(OH)_2 = CaCO_3 \text{ (insoluble)} + H_2O$$

$$CaCO_3 + H_2O + CO_2 \rightleftharpoons Ca(HCO_3)_2 \text{ (soluble)}.$$

(b) The gas reacts with caustic soda, giving a solution of sodium carbonate, but with excess of the gas *sparingly* soluble sodium bicarbonate is produced, which on heating gives pure carbon dioxide.

$$2NaOH + CO_2 = Na_2CO_3 + H_2O\ ;\ Na_2CO_3 + H_2O + CO_2 \rightleftharpoons 2NaHCO_3.$$

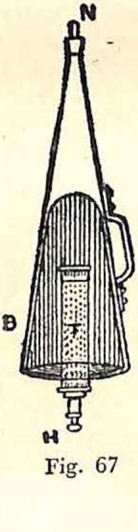


Fig. 67

(viii) The gas is decomposed by the green colouring matter of plants, known as *chlorophyll*, in presence of sunlight and moisture into carbon, which is assimilated by plants, and oxygen which is set free. The process is known as *photosynthesis*.

Tests.—Like nitrogen, the gas neither burns nor supports combustion ; but unlike nitrogen, it turns lime water milky.

Uses.—(i) In the manufacture of sodium carbonate by Solvay's process, urea and salicylic acid; in the refining of sugar.

(ii) As a refrigerant as **dry ice** (also called dri-cold), it is so called, since it does not melt to water, as ice does, but evaporates. Carbon dioxide is liquefied under a pressure of 1000 lbs. per sq. in.—the liquid on evaporation solidifies to 'carbon dioxide snow', called *dry ice* which is used for cooling ice creams, packing fish, etc. The dry ice sublimes at −79°. Liquid carbon dioxide is sold in steel cylinders.

(iii) In extinguishing fire. **A fire extinguisher** (fig. 67) consists of a metal casing B containing a solution of sodium carbonate, with a glass bottle T. of sulphuric acid inside. The bottle may be broken by a rod attached to a knob H outside—the acid coming in contact with the carbonate liberates carbon dioxide which is directed against fire from a nozzle.

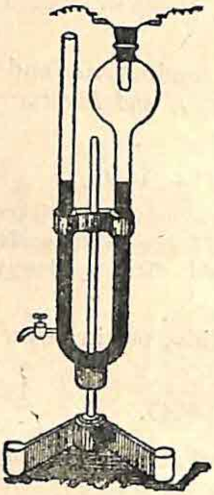


Fig. 68

(iv) In the preparation of 'aerated waters' such as lemonade and soda water which are solutions of carbon dioxide under pressure ; and as a leavening agent. *Baking powder* contains sodium bicarbonate and tartaric acid, which do not react when dry. In presence of water, sodium tartrate is formed and CO_2 is evolved, the bubbles of which are expanded by heat on baking.

(v) In medicine and first aid in cases of shock, gas poinsoning and asphyxiation. A mixture 95 per cent O_2 and 5 per cent CO_2 is administered by gas mask and forced respiration in order to stimulate natural respiration.

Volumetric composition.—The volumetric composition of the gas is established by burning a piece of pure sugar charcoal in a confined volume of oxygen over mercury—the experiment showing that carbon dioxide contains its own volume of oxygen. The apparatus consists of a U-tube (fig. 68) ending in a bulb at one end, which is provided with a glass-stopper through which pass two copper wires, one of of which ends in a metal spoon. The two wires are connected by a platinum spiral, touching a piece of pure sugar charcoal on the spoon. The bulb and a part of the limb is filled with oxygen at atmospheric pressure by the displacement of mercury, and the charcoal is ignited by passing electric current through the spiral. Carbon is burnt into carbon dioxide. On cooling the apparatus, mercury is found to stand at the same level as before, i.e., no change in volume has taken place in the conversion of carbon into carbon dioxide. Hence *carbon dioxide contains its own volume of oxygen*, i.e. 1 volume of carbon dioxide contains 1 volume of oxygen.

Let 1 volume of carbon dioxide contain n molecules of carbon dioxide, then 1 vol. of oxygen also contains n molecules of oxygen by Avogadro's hypothesis. Therefore, n molecules of carbon dioxide contain n molecules of oxygen or 1 molecule of the gas contains 1 molecule (i.e., 2 atoms) of oxygen (by Avogadro's hypothesis). Hence the formula is CxO_2 and the molecular weight $= 12x+2\times16$. But the mol. wt. is 44, its vapour density being 22, found experimentally i.e., $12x+2\times16=44 \therefore x = 1$ and the formula of carbon dioxide is CO_2.

Coal gas.—Coal gas is the gaseous product, mainly a mixture of combustible gases, produced by the carbonisation (destructive or dry distillation) of coal. Its approximate average composition in percentage by volume is :

(i) *Non-illuminating but heat producing*	: hydrogen	...	45—50
	methane	...	30—50
	carbon monoxide		5—10
(ii) *Illuminants (unsaturated hydrocarbons)*	: ethylene, acetylene and benzene	...	2.5—5
(iii) *Diluents (inerts)*	: nitrogen	...	2—10
	carbon dioxide	...	0—2
	oxygen	...	0—1
(iv) *Impurities*	: hydrogen sulphide, etc, if any		

Besides the coal gas, other products (i.e. by-products) of distillation of coal are tar, ammoniacal liquor, coke and gas carbon.

Coal gas was first obtained by Rev. John Clayton in 1688 by the destructive distillation of coal but it was first introduced as an illuminant by William Murdock in 1792.

In gas-works practice only bituminous coal is carbonised. Powdered bituminous coal is distilled in a row of horizontal fire clay retorts, externally heated by the combustion of producer gas in a furnace (fig. 69)—the temperature being 1000° to 1200°C. The volatile products given off are led by vertical iron ascension pipes

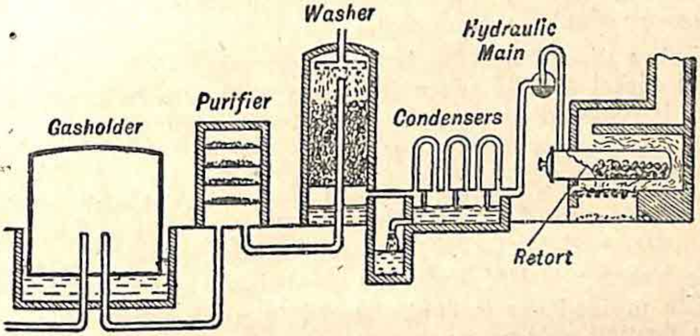


Fig. 69

from the retorts into a long horizontal tube, called *hydraulic* main, which acts as a water-seal, preventing any gas escaping when the retort doors are opened for recharging. In the hydraulic main partial separation into crude gas, tar and ammoniacal liquor occurs. Much tar and ammoniacal liquor separate and is deposited in the hydraulic main where the temperature is about 60° only. The gas leaving the main contains traces of H_2S, NH_3, HCN, and CS_2 as impurities. The gas next passes through :

(i) a series of air or water-cooled iron pipes, called *condensers*, where it is cooled to atmospheric temperature and hence more tar and ammoniacal liquor separate and collect in the tar well in two layers—the top layer being ammoniacal liquor and the bottom layer tar :

(ii) a rotary *suction pump* (*exhauster*) which drives the gas forward through the subsequent purifiers into the gas holder. From the exhauster the gas passes to :

(iii) *a tar separator* in which any accompanying tar fog separates and deposits as droplets. The gas then passes through :

(iv) an iron tower (called a washer or *scrubber*) which is packed with coke, and down which a stream of water trickles—all traces of tar and ammonia are washed away with water in the scrubber. The scrubbed gas still contains H_2S and CS_2 as impurities, and passes to :

(v) the *purifier* which are iron boxes containing hydrated ferric oxide spread on shelves. Ferric oxide reacts with the hydrogen sulphide, forming ferric sulphide :

$$2Fe(OH)_3 + 3H_2S = Fe_2S_3 + 6H_2O.$$

The oxide is revived by exposure to moist air, when sulphur is separated and hydrated ferric oxide is regenerated, to be used over again : $2Fe_2S_3+6H_2O+3O_2=4Fe(OH)_3+6S$.

When the iron oxide contains about 50% free sulphur, it is used as a source for sulphur for making sulphuric acid, and is then known as *spent oxide of iron*. Purification of coal gas thus offers a method of recovery of sulphur from coal.

Carbon disulphide CS_2, is then removed by passing the gas over heated nickel at 430° when it is converted into hydrogen sulphide which is removed as usual by moist ferric oxide :

$$CS_2+2H_2=C+2H_2S.$$

Sometimes H_2S is absorbed by slaked lime, when carbon disulphide is also simultaneously removed as calcium thiocarbonate.

$$Ca(OH)_2+2H_2S=Ca(SH)_2+2H_2O\ ;\ Ca(SH)_2+CS_2=CaCS_3+H_2S.$$

The hydrogen sulphide liberated is absorbed in a second lime purifier.

The purified gas is finally stored in gas-holders, which are iron tanks floating on iron or masonry trough, containing water, by the aid of weights suspended by pulleys.

The weight of coal gas obtained is about 17% of the weight of coal carbonised, i.e., about 380 lbs. per ton of coal. The tar, ammoniacal liquor and coke form 5%, 8% and 70% respectively, of the weight of coal.

Coal gas burns with a smoky flame, forming CO_2 and H_2O. It is a colourless gas with a peculiar smell and possesses reducing properties. Its calorific value is about 560 B.Th.U. per cubic foot.

Coal gas finds extensive use as an illuminant in cities and towns—Welsbach mantle which contains thoria and 1 or 2 per cent ceria, is heated to incandescence in gas light. It is also used as a fuel. Coal gas also finds use in metallurgy.

By-products of the coal gas industry.—(i) **Coal tar :** On fractional distillation it gives benzene, toluene, naphthalene, carbolic acid, creosote oil, etc. which are the starting materials for obtaining numerous dyes, drugs, perfumes and explosives. The coal tar pitch is used for road making. Coal tar directly or the creosote oil is used for preserving timber, water-proofing gunny bags, etc.

(ii) **Ammonical liquor :** On boiling with milk of lime it yields ammonia which is usually fixed by sulphuric acid as *ammonium sulphate* to be used as a fertiliser.

(iii) **Coke :** This is a residue left in the retort after the distillation of coal and is extensively used as a domestic fuel and in metallurgy.

(iv) **Gas carbon :** It is obtained as a hard dense deposit inside the retort due to the thermal decomposition of gaseous hydrocarbons in contact with the hot walls of the retort. A good conductor of heat and electricity, it is used in making electrodes.

(v) **Spent iron oxide :** It contains sulphur and cyanogen compounds and is used for the preparation of potassium ferro-cyanide and for the recovery of sulphur. **Gas lime** (or **spent lime**) from the purifier is used as a manure.

Crude benzene is nowadays extracted from coal gas by washing with a suitable oil, and is recovered ; the naphthalene vapour present in the coal gas (which tends to deposit as a solid in the pipes) is also taken out by this process.

Exercises

1. What is meant by allotropy ? Give an account of the different allotropic forms of carbon. How would you establish that diamond is nothing but carbon ?

How would you show that all the allotropes of carbon are one and the same element ?

2. Describe the preparation of carbon dioxide in the laboratory. Mention its chief properties, tests and uses. Derive the formula of the gas from its volumetric composition.

3. (i) Describe the changes that occur when carbon dioxide is passed into : (a) lime water, (b) caustic soda solution.

(ii) What happens when : (a) a piece of burning magnesium is inserted into a jar of carbon dioxide, (b) carbon dioxide is passed over red hot charcoal ?

(iii) How would you show that carbon dioxide contains carbon ?

4. Give an outline of the distillation of : (i) coal, (ii) wood. Mention the chief products of distillation and state their important uses. *P. U.* 61

5. (i) What is pyroligneous acid ? Indicate its chief constituents and mention their uses.

(ii) State the uses of : ammoniacal liquor, wood charcoal, spent iron oxide, and wood tar.

6. What is coal gas ? What are its main constituents ? Describe the preparation and purification of the gas. What are the by-products of coal gas manufacture ? State their principal uses.

XVIII

METALS AND METALLIC COMPOUNDS

Metals are in the service of man from prehistoric days. Our material civilisation has beeen largely due to our knowledge and application of metals. The 'bronze age', in human history followed the 'stone age' and preceded the present 'age of steel'. About seventy-four of the elements are metals.

Metals are generally found in nature as natural materials, called **minerals,** usually in the form of oxides (e.g., hæmatite, cassiterite, and bauxite, etc), sulphides (e.g., zinc blende, galena, cinnaber, and copper pyrites, etc.), carbonates (e.g., limestone, magnesite, and dolomite, etc.), and silicate (e.g., felspar, mica, and kaolin, etc.), etc. A few metals, such as copper, gold and platinum, are sometimes found as such in nature, and are then said to occur *native.*

Metallurgy : *The winning and refining of metals.*—Metals are obtained from ores. **An ore** is a mineral that may be profitably and conveniently treated for the extraction of one or more metals.

Metallurgy is the science and art of winning (or extracting) a metal from its ore.

The method of winning metals from ores varies with the particular metal and the nature of ores. Native copper, gold and platinum are worked up by refining only.

Important processes for the extraction of metals include :

(i) **The carbon-reduction process.**—The process involves the reduction of a compound of the metal, the ore, to the free metal. The principal reducing agent is carbon, usually in the form of coke. A typical procedure for the treatment of ores, consists of the following operations : (a) *crushing* and *grinding*, (b) *concentration*, (c) *calcination* or *roasting*, (d) *smelting* or *reduction*.

(a) **Crushing and grinding.**—The ore, usually found as a rock mass, is first crushed to pieces,—a *stone-breaker*, *jaw crusher*, *grinding mill* or *stamps* being employed according to the degree of fineness required. The broken staff is then separated into sizes by a series of screens.

(b) **Concentration of the ore,** also called **dressing the ores,** The ore generally contains rocky impurity, such as silica and silicates called **gangue** or **matrix.** Hence the necessity of dressing the ores before calcination and smelting. One or more of the following operations are usually employed.

(i) **Gravity separation.**—The crushed ore is washed in a current of water which carries away the light sileceous gangue, leaving the heavy ore behind ; the process is used in concentrating the tin ore, cassiterite.

(ii) **Magnetic separation.**—Many ores differ in magnetic property from rocky impurity ; magnetic wolfram is removed from non-magnetic cassiterite by electromagnetic separation.

(iii) **Oil-floatation process.**—The process works particularly well with *the sulphide ores*, and is used in concentrating copper pyrites, galena, and blende. The crushed ore is churned up with water containing a little oil, such as pine and eucalyptus oils, which wets the ore but not the gangue—the ore therefore, collects in the froth formed on the surface of the liquid, and is removed ; the gangue is wetted by water and consequently sinks to the bottom. The ore is separated from the froth. Thus the *ore concentrate* is obtained.

(c) **Calcination and roasting.**—*Roasting* is a process of heating the ore *without fusion in a plentiful supply of air* in order to *oxidise* it. *Calcination* means heating the ore in air without fusion, the purpose being to drive off moisture and volatile matter from the ore. But the two terms are often used in the same sense ; roasting, however, usually involves higher temperature than calcination. Moisture, carbon dioxide and impurities, such as arsenic, which form volatile oxides, are eliminated during calcination. The calcined material is in a *porous state*, and is therefore readily reduced during smelting.

The ore concentrates are, usually, subjected to calcination ; the oxide minerals cassiterite and haematite, for example, are calcined. The carbonate minerals, such as magnesite, $MgCO_3$, and *siderite*, $FeCO_3$, are calcined to their oxides :

$$MgCO_3 = MgO + CO_2 ; \qquad FeCO_3 = FeO + CO_2.$$

Ferrous oxide is converted to the ferric state during calcination.

The *sulphide minerals, such as blende* and *galena,* are roasted in air and *sintered* with incipient fusion at high temperatures in order to convert them to oxides :

$$2ZnS + 3O_2 = 2ZnO + 2SO_2 ; \quad 2PbS + 3O_2 = 2PbO + 2SO_2.$$

(d) **Smelting** or **reduction.**—The calcined ore containing metallic oxide, mixed with carbon and flux, is smelted in a furnace, when the oxide is reduced to the metal—*smelting* is an operation whereby the metal is separated *by fusion* from the ore.

A **flux** is a substance added to the furnace charge to remove the gangue forming a fusible body, called a *slag* or *cinder ;*

flux + gangue = slag.

The selection of flux depends upon the nature of the gangue ; it must be acid to remove basic impurities, and basic for acid impurities. In the smelting of iron the acid gangue silica is fluxed with lime, yielding a slag of calcium silicate, while in the extraction of copper ferrous oxide is removed as a slag of ferrous silicate by adding the acid flux silica.

$$CaO+SiO_2 = CaSiO_3 ; \quad SiO_2+FeO = FeSiO_3$$

The molten slag floats on the surface of liquid metal (and hence protects it from the action of air), forming an immiscible layer which can be easily drawn off.

The metals below aluminium in the electro-chemical series are usually obtained by the reduction of their oxides with carbon ; e.g., *zinc, iron, tin, lead,* and *copper.* The oxides of aluminium and metals above it in the series (*except magnesium*) are too stable to be reduced by carbon ; these metals are therefore, obtained by electrolytic methods. Magnesium oxide is, however, reduced by carbon at the high temperature of electric furnace.

(ii) **The self-reduction process.**—As already stated above the sulphide ores are roasted and sintered into oxides, which are then smelted with carbon, e.g., zinc blende and galena. But it is often *partially* roasted, and the oxide or sulphate produced is reduced by the unchanged sulphide during smelting. This is a *self-reduction process,* since the reduction takes place by the sulphide itself :

$$2PbS+3O_2 = 2PbO+2SO_2 ; \quad PbS+2O_2 = PbSO_4$$
$$2PbO+PbS = 3Pb+SO_2 ; \quad PbS+PbSO_4 = 2Pb+2SO_2.$$

Copper and lead are made by the self-reduction process.

The metals, of which the oxides readily lose oxygen, can be obtained by simple roasting or by smelting with lime :

$$HgS+O_2 = Hg+SO_2 ; \quad 4HgS+4CaO = 4Hg+3CaS+CaSO_4.$$

Sulphide minerals can be reduced by iron, which is converted into iron sulphide :

$$Sb_2S_3+3Fe = 2Sb+3FeS ; \quad HgS+Fe = Hg+FeS.$$

(iii) **The thermit process.**—Some metals, e.g., Cr and Mn, are made by reduction of their oxides with a more active metal, e.g., aluminium.

$$Cr_2O_3+2Al = 2Cr+Al_2O_3 ; \quad 3Mn_3O_4+8Al = 9Mn+4Al_2O_3.$$

(v) **The electrolytic method.**—The alkali and alkaline earth metals are too strongly electro-positive (standing at the head of the electro-chemical series) to be made by the electrolysis of the aqueous solutions of their salts ; they are obtained by the electrolysis of *fused chlorides ;* e.g., *sodium*, *potassium*, *calcium*, and *magnesium*. Fused hydroxide is also used for sodium and potassium.

Aluminium is also too electro-positive to be separated from the aqueous solution. It is made by the electrolysis of aluminium oxide dissolved in a bath of molten cryolite and fluorspar.

Metals below aluminium in the series may also be isolated by the electrolysis of an aqueous solution. The process is used for obtaining copper and zinc (*wet process of metallurgy*). The electrolytic method is generally applied for the refining of metals ; e.g., *copper*, *silver*, *nickel*, *tin* and *lead*.

The Alkali Metals.—*Natron* (natural sodium carbonate) and wood ashes were used by the ancients as detergents for washing clothes. Potassium carbonate was extracted from wood ashes by water by the Arabs, and was called *al quali*, whence was derived the name *alkali* for sodium and potassium carbonates. It was discovered in the Roman period that the natural alkalis were rendered *highly corrosive and caustic* by boiling with lime, and hence the name *caustic alkalis* for sodium hydroxide (caustic soda) and potassium hydroxide (caustic potash). Just to distinguish from caustic alkalis, sodium and potassium carbonates were called *mild alkalis*.

Davy isolated (1807) the alkali metals sodium and potassium by the electrolysis of fused caustic soda and potash respectively.

Sodium

Density 0.97, m.p. 97.5°C, b.p. 880°C, atomic weight 22.997.

Occurrence.—Sodium is one of the most abundant elements, but it is never found free in nature. Its more important naturally-occurring compounds are : (i) *sodium chloride*, $NaCl$, in sea-water and as rock-salt, (ii) *sodium nitrate*, $NaNO_3$, in Chile saltpetre, (iii) *sodium carbonate*, Na_2CO_3. Deposits of sodium sesquicarbonate, Na_2CO_3, $NaHCO_3$, $2H_2O$, occur in lake Magadi in East Africa, in Egypt, as *trona* and also in India as native *sajimati*, (iv) *soda felspar*, Na_2O, Al_2O_3, $6SiO_2$, and (v) *borax*, $Na_2B_4O_7,10H_2O$.

Though first isolated by Davy (1907) by the electrolysis of fused caustic soda, sodium was for many years made by heating caustic soda with carbon and iron at 1000°C for want of cheap electricity.

$$2NaOH + 2C = 2Na + 2CO + H_2.$$

Metallic sodium.—Metallic sodium is now obtained by the electrolysis of either *fused caustic soda* or *sodium chloride*.

(i) **Castner process.**—In this process *fused* caustic soda is electrolysed using a *steel cathode* and a *nickel anode*. The caustic soda ionises into sodium and hydroxyl ions. During electolysis sodium ions are discharged at the cathode as metallic sodium, and the OH ions at the anode as OH groups which readily decompose into water and oxygen, the latter being evolved at the anode.

$$NaOH \leftrightharpoons Na^+ + OH^- \; ; \; Na^+ + e = Na$$
$$OH^- = OH + e \; ; \qquad 4OH = 2H_2O + O_2.$$

Some of the water formed diffuses across to the cathode and attacks sodium, yielding hydrogen—the efficiency of the process is being lowered thereby, since some sodium is lost. But the principal disadvantage of the process is the relatively high cost of caustic soda.

An iron vessel (fig. 70) contains the caustic soda which is fused initially by gas burners (m. pt. of sodium hydroxide 318°), but the process of electrolysis once started, the required temperature of the bath, 327°, is maintained by the heating effect of the current. The steel cathode is led into the bath from below and held in position in the neck of the pot by solid caustic soda; the cathode is screened by an iron wire gauze, suspended from an iron cylinder. The anode is a nickel cylinder that surrounds the cathode and forms a part of the cover, being insulated by asbestos rings from the iron bath, and from the iron cylinder in which sodium collects. During electrolysis sodium is liberated at the cathode and collects in the iron cylinder in the molten state, floating on the surface of molten caustic soda—the hydrogen, also collecting in the same vessel, prevents the sodium from oxidation. Sodium is removed from time to time by means of a spoon of nickel wire gauze which retains the sodium but allows the caustic soda to run back. The oxygen liberated at the anode is a valuable by-product.

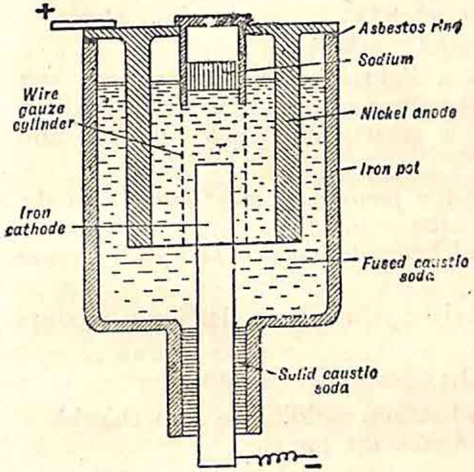


Fig. 70

(ii) **Downs process.**—Sodium chloride is the cheapest source of sodium. But the electrolysis of fused sodium chloride is ordinarily met with many difficulties arising from its high melting point, 803°. Above 800° the sodium chloride and the liberated chlorine are highly corrosive, and the sodium is volatile (b. pt. 880°), and the metal forms a 'metallic fog' with the molten salt, which it is difficult to condense. In the Downs process, worked out in 1924 by Downs in America, fused sodium chloride, containing sufficient calcium chloride to reduce the melting point of the salt from 800° to 650° at which temperature no 'metallic fog' formation takes place, is electrolysed in an iron vessel (fig. 71) lined inside with firebricks. Chlorine is evolved at the graphite anode set in the centre of the cell, and is led out by a conical collecting hood which is placed above the anode.

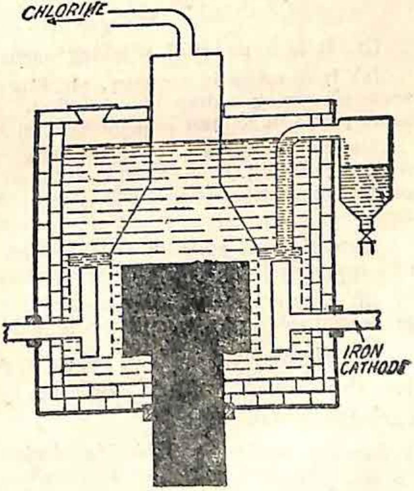


Fig. 71

The cathode is an iron cylinder surrounding the anode—a mantle of two iron-gauge screens separates the anode from the cathode. The sodium set free at the cathode rises to the surface of the electrolyte and is led by an iron pipe, fitted at the top of the mantle, into a closed receiver

$$NaCl \rightleftharpoons Na^+ + Cl^-.$$

At cathoe $Na^+ + e = Na$; At anode $Cl^- = Cl + e$.

Properties.—(i) Sodium is a light (lighter than water), soft (and hence may be squeezed through an orifice in the form of sodium wire), silver-white metal with a good conductivity for heat and electricity.

(ii) Stable in dry air, it readily *tarnishes in moist air* due to the formation of a film of oxide, which gradually turns into a mixture of hydroxide and carbonate, and hence *the metal is kept under kerosene oil.*

(*iii*) It burns in air with a bright *yellow flame*, yielding a mixture monoxide and peroxide :

$$4Na + O_2 = 2Na_2O \; ; \; 2Na + O_2 = Na_2O_2.$$

(iv) It burns in chlorine on heating, yielding sodium chloride—perfectly *dry* chlorine does not attack the metal.

(v) It decomposes cold water, yielding hydrogen and caustic soda : $2Na + 2HOH = 2NaOH + H_2$.

(vi) It reacts with dry ammonia at 300° to 400°, yielding *sodamide*, $NaNH_2$, which is decomposed by water, liberating ammonia :

$$2Na + 2NH_3 = 2NaNH_2 + H_2 \; ; \; NaNH_2 + H_2O = NaOH + NH_3.$$

(vii) It reacts with hydrogen at 360°, yielding *sodium hydride*, which is decomposed by water, setting free hydrogen :

$$2Na + H_2 = 2NaH \; ; \quad NaH + HOH = H_2 + NaOH.$$

(viii) Ignited sodium decomposes carbon dioxide, depositing carbon :

$$3CO_2 + 4Na = 2Na_2CO_3 + C.$$

(ix) It is a powerful reducing agent : $3Na + AlCl_3 = Al + 3NaCl$.

(x) It dissolves in mercury, yielding a liquid amalgam. It dissolves in liquid ammonia giving a deep blue solution. Sodium amalgam is prepared by pressing small pieces of sodium into mercury in a mortar with a pestle.

Uses of sodium.—(i) In the manufacture of sodium peroxide, sodamide, and sodium cyanide ; (ii) As a reducing agent in synthetic organic chemistry, for example in the manufacture of artificial *indigo*. Sodium amalgam is also used as a reducing agent.

Detection of sodium.—(i) Sodium compounds give a golden yellow flame, and hence may be detected by *flame test*.

(ii) Zinc uranyl acetate gives a yellow precipitate of sodium zinc uranyl acetate in neutral solution. Magnesium uranyl acetate also gives a similar precipitate.

Sodium hydroxide, caustic soda, $NaOH$, is manufactured either by the electrolysis of sodium chloride or by causticising sodium carbonate with lime.

Electrolysis of sodium chloride solution yields caustic soda, hydrogen and chlorine (p. 85). Sodium hydroxide and hydrogen formed at the cathode must be kept separated from chlorine produced at the anode, in order to prevent the formation of hydrochloric acid and of explosive mixture of hydrogen and chlorine. The separation is effected either *by using a mercury cathode* or *a porous diaphragm.*

The mercury cathode cell.—In the *Kellner-Solvay* cell (fig. 72) (modified *Castner-Kellner cell*) a stream of brine (aqueous solution of sodium chloride) is electrolysed between graphite anode and a mercury cathode, which flow slowly in thin layer across the floor of the cell (a rectangular cement trough)—brine flows in the same direction as the mercury. Chloride ions Cl' are discharged at the anode to form chlorine which is drawn away through earthenware pipes to be liquefied or used in making HCl, bleaching powder and sodium hypochlorite etc. Na^+ ions are discharged at the cathode in preference to H^+ ions, yielding sodium, which dissolves in mercury to form a dilute liquid sodium amalgam.

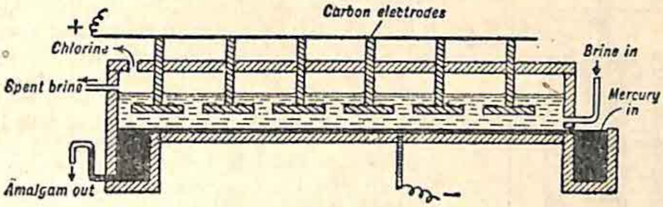


Fig. 72

The sodium amalgam flows into a lower tank, where it is decomposed by water, yielding caustic soda and hydrogen, in contact with metallic iron—the amalgam and iron forming a short-circuited cell :

$$^-\text{Na-amalgam—NaOH solution—Fe}^+$$

Sodium from the amalgam passes into solution as sodium ions : $Na = Na^+ + e$, and the electrons pass through the mercury to the iron ; the hydrogen ions from water ($H_2O \rightleftharpoons H^+ + OH'$) are discharged by the electrons on the iron surface, which evolve as gas :

$$H^+ + e = H\ ;\quad 2H = H_2.$$

The overall reactions are :

In the primary cell, $2NaCl + 2xHg = 2NaHgx + Cl_2$.

In the secondary cell, $2NaHgx + 2H_2O = 2NaOH + H_2 + 2xHg$.

The solution, therefore, contains Na^+ and OH' ions, i.e., sodium hydroxide. When the solution contains 40% caustic soda, it is evaporated, fused, and run into iron drums to solidify or cast into sticks. The mercury freed from the sodium is sent back, into the electrolytic cell.

The spent brine is saturated with more salt, and then returned to the cell.

The diaphragm cells.—Typical of this class is the Nelson cell which is extensively employed. It consists of a U-shaped vessel (fig. 73) made of asbestos and contains the graphite anode. The cathode is made of perforated sheet steel covering the outer surface of the asbestos walls, which constitute the diaphragm. The cell is placed in an outer case, which is kept full of steam—the steam heats the liquor, reduces its resistance, and also keeps the pores of the diaphragm clear. The cell is fed with *purified* brine, which is kept at a constant level by an auto matic device—the brine must be freed from salts of iron and other metals which would give insoluble hydroxides with caustic soda, and so clog the diaphragm. The brine percolates by gravity through the asbestos, where it undergoes electrolysis. The Cl' ions are discharged at the anode and the chlorine gas is led off. H^+ ions are discharged at the cathode, where Na^+ and OH^- ions, i.e., sodium hydroxide, accumulate in the water which diffuses through the porous diaphragm from the anode compartment. The alkali concentration is only 10—12%, the liquor containing 14—16% NaCl, which is separated as solid by concentration in vacuum evaporators, and the concentrated caustic liquor finally evaporated and fused.

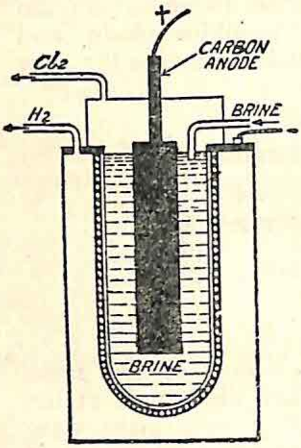


Fig. 73

Causticising of sodium carbonate.—Gossage's method : When calcium hydroxide is added to sodium carbonate solution, calcium carbonate is precipitated, leaving sodium hydroxide in solution :

$$Na_2CO_3 + Ca(OH)_2 \rightleftharpoons 2NaOH + CaCO_3.$$

The reaction is incomplete in concentrated solutions, since calcium hydroxide is but sparingly soluble in a strong solution of caustic soda : *a dilute solution* of sodium carbonate is, therefore, causticised. On a large scale, a 10% solution of soda ash is taken in an iron tank—lumps of lime are suspended in the solution in an iron cage. The solution is stirred by mechanical agitators, and heated by *open* steam. The reaction complete in about an hour's time, the sludge of chalk and excess lime is allowed to settle, and the clear caustic liquor is run off. The liquor is concentrated in vacuum evaporators, where the unchanged sodium carbonate separates and is removed. The concentrated sodium hydroxide solution is evaporated to dryness, fused and run into drums to solidify.

A large amount of caustic soda is still obtained by this process, since its production by electrolytic method is limited by the demand for chlorine.

Purification of sodium hydroxide.—Sodium hydroxide obtained by the above methods is liable to contain sodium chloride, carbonate, and sulphate in small amounts. This is purified by treatment with alcohol which dissolves the hydroxide, but not the salts, and then evaporating the solution in a silver dish. Pure caustic soda free from sodium carbonate is best obtained by dissolving sodium in water.

Properties.—(i) Sodium hydroxide is a white, crystalline, deliquescent, highly corrosive solid (m. p. 318°), which readily absorbs CO_2 from the air, forming sodium carbonate. *A powerful cautery*, it attacks the proteins of the skin.

(ii) *Stable towards heat*, it is reduced in the fused state to metal, when heated with carbon : $2NaOH + 2C = 2Na + 2CO + H_2$.

The presence of hydrogen in caustic soda (or potash) may be shown by fusing the latter with iron filings in a test tube—the evolved hydrogen being ignited at a jet fixed to the tube. The iron is oxidised and sodium also distils off :

$$2NaOH + 2Fe = 2FeO + 2Na + H_2.$$

(iii) *A strong base*, it readily dissolves in water (42 gms. in 100 gms. of water at 0°) giving a strongly alkaline solution with a soapy touch. The aqueous solution precipitates the hydroxides or oxides of heavy metals, from solutions of their salts, and liberate ammonia from ammonium salts :

$$FeCl_3 + 3NaOH = Fe(OH)_3 + 3NaCl\ ;$$
$$NH_4Cl + NaOH = NaCl + NH_3 + H_2O.$$

The hydroxides of Zn, Al, Sn, and Pb are soluble in excess of caustic soda :

$$Zn(OH)_2+2NaOH = Na_2ZnO_2 \text{ (sodium zincate)}+2H_2O.$$

(iv) It dissolves acidic and amphoteric oxides, yielding salts :

$$CO_2+2NaOH = Na_2CO_3+H_2O \text{ ;}$$
$$Al_2O_3+2NaOH = 2NaAlO_2+H_2O.$$

Materials containing *silica*, such as *glass*, are rapidly attacked by fused caustic soda, and slowly by aqueous alkali, silica being dissolved as sodium silicate :

$$SiO_2 + 2NaOH = Na_2SiO_3 + H_2O.$$

(v) Aqueous sodium hydroxide dissolves B, Si, Zn, Al and Sn, yielding salt and hydrogen ; several non-metals, such as P, S, Cl, etc., yield a hydride (or a salt of the hydride) instead of hydrogen.

$$4P+3NaOH+3H_2O = PH_3+3NaH_2PO_2 \text{ (sodium hypophosphite).}$$
$$2Al+2NaOH+2H_2O = 3H_2+2NaAlO_2 \text{ (sodium aluminate).}$$

Nearly all metals are attacked by fused caustic alkali ; Fe, Ni, Ag, Au and Pt are the most resistant to attack.

Uses of sodium hydroxide.—It is used : (i) in the manufacture of sodium, soap and sodium formate ; (ii) in the purification of bauxite ; (iii) in the manufacture of paper, artificial silk and dyes ; (iv) in the refining of petroleum ; (v) in making alkaline bleach ; (vi) as a cleansing agent for machines, metal sheets, etc., since it emulsifies oil and grease ; *it is too caustic for use in washing.*

Sodium carbonate, Na_2CO_3.—It occurs in and around certain lakes, notably at Magadi in East Africa, and in Lower Egypt. The Magadi deposit, containing some 200 million tons of native soda, forms an important source of soda supply.

Sodium carbonate was formerly obtained from the ash of plants growing on sea-shore. But the method was superseded early in the nineteenth century by the *Leblanc process*, discovered by Nicholas Leblanc in 1787, as a result of an offer of prize by the French Academy of Science for the preparation of alkali from common salt.

The Leblanc process.—The main features of the process are :

(i) **Production of salt cake.**—Sodium chloride is converted to sodium sulphate called *salt-cake*, by heating with concentrated sulphuric acid in a furnace.

$$NaCl + H_2SO_4 = NaHSO_4 + HCl$$
$$NaCl + NaHSO_4 = Na_2SO_4 + HCl$$

The HCl gas is absorbed by water giving hydrochloric acid.

(ii) **Conversion of salt-cake into black ash.**—The salt cake is strongly heated with limestone and coal, in a furnace, when it is converted into sodium carbonate and calcium sulphide :

$$Na_2SO_4 + 4C = Na_2S + 4CO \text{ ; } \quad Na_2S + CaCO_3 = Na_2CO_3 + CaS.$$

The product is called *black ash* and contains 45% sodium carbonate.

(iii) **Lixiviation of black ash.**—The black ash is lixiviated with water. The extract contains sodium carbonate. It is concentrated by heat and crystallised out as soda crystals or washing soda, $Na_2CO_3,10H_2O$; the soda crystals on calcination gives anhydrous sodium carbonate, soda ash.

The alkali waste, left after extracting soda, contains calcium sulphide, and may be used for sulphur recovery.

The Leblanc process as a whole is obsolete ; only the first step is worked to provide salt-cake (sodium sulphate) for glass making.

The Ammonia-soda process, or **Solvay process.**—About the middle of the nineteenth century the Solvay process gradually became a serious rival of the Leblanc process, which it ultimately displaced. Nearly all the sodium carbonate is now manufactured by the Solvay process.

The principle of the process is that, when an excess of carbon dioxide is bubbled through nearly saturated solution of common salt (brine) containing ammonia, ammonium bicarbonate is formed; this then reacts with the sodium chloride yielding *sparingly soluble sodium bicarbonate* and ammonium chloride. The sodium bicarbonate is separated by filtration and calcined to give sodium carbonate and and carbon dioxide.

$$NH_3+CO_2+H_2O \rightleftharpoons NH_4HCO_3\ ;$$
$$NH_4HCO_3+NaCl \rightleftharpoons NaHCO_3+NH_4Cl.$$
$$2NaHCO_3=Na_2CO_3+H_2O+CO_2$$

About two-thirds of the common salt is converted into sodium bicarbonate, as the reaction is reversible.

The ammonium chloride in the filtrate is boiled with lime in a still to regenerate ammonia, which is used again to saturate fresh brine.

$$2NH_4Cl + Ca(OH)_2 = 2NH_3 + 2H_2O + CaCl_2.$$

The lime is obtained by heating limestone with coke in a kiln. $CaCO_3=CaO+CO_2$. The CO_2 produced, together with that obtained by calcining sodium bicarbonate, is used for carbonating ammoniacal brine.

The process depends upon the supply of the raw materials brine, limestone and coal. The process is carried out as follows:

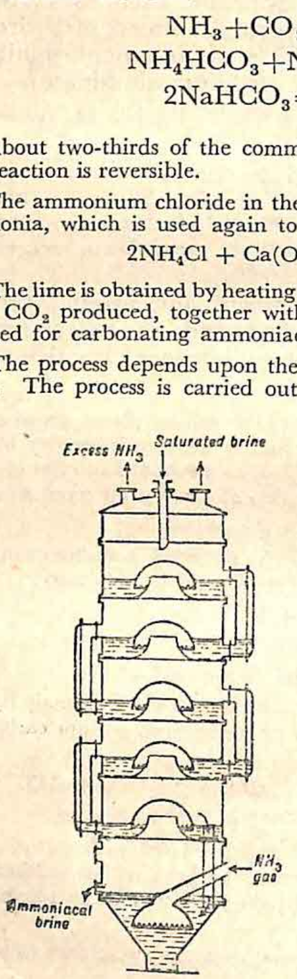


Fig. 74

(i) **Preparation of ammoniacal brine.**—The brine trickles down a a tower (fig. 74) fitted with a number of partitions, in which ammonia enters at the bottom.

The brine forms a layer on the floor of each compartment and flows down vertical pipes from one compartment to the next below; ammonia is made to pass up the centre of the tower, and stream through the brine on each floor by means of a series of hoods. The brine gets saturated with ammonia, and at the same time *salts of Ca*, *Mg* and *Fe* present in the brine are precipitated as carbonates by carbon dioxide (always contained in the ammonia from the still). The ammoniacal brine, passing out at the bottom, is allowed to settle out in a settling tank, whence it is led to a *cooler*, and then to the carbonating tower.

(ii) **Carbonation.**—The carbonation is carried out in Solvay's tower (fig. 75) which is fitted with a number of paritions, each having a central hole covered by a perforated hood. The ammoniacal brine is introduced at the top so as to *completely fill* the lower part of the tower, and carbon dioxide is forced under pressure at the base. The carbon dioxide is uniformly distributed through the solution in small bubbles, and a perfect absorption takes place. Heat is evolved in the reaction, and since the solubility of bicarbonate increases with rise in temperature, the tower is cooled by circulation of cold water through coils fitted in the lower part—the temperature is kept at 30°-40°, but is reduced to about 15° towards the end. The sodium bicarbonate precipitates and passes out with solution at the base.

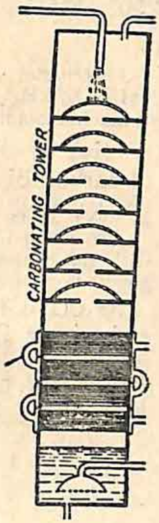


Fig. 75

(iii) **Filtration.**—The sodium bicarbonate is separated by filtration by a *rotary suction filter* which is essentially a sheet of flannel stretched on a wire-gauze drum ; the drum is half submerged in the solution and kept in slow rotation—vaccum being maintained on the inside. The bicarbonate deposits on the flannel : It is scrapped out after washing with a spray of water, and then dried.

(iv) **Calcination.**—The bicarbonate is calcined in a closed pan fitted with an exit to remove carbon dioxide. The last traces of CO_2 are removed by raking the calcined mass through a long trough heated by fire below. The *soda ash*, thus produced, is of 99.5 per cent purity.

Advantage of the Solvay process.—The Solvay process has completely displaced the old Leblanc process, since

(i) it delivers soda of much higher purity ;

(ii) the process is less expensive, since brine is directly used, and no sulphuric acid is required ;

(iii) the operation is continuous, and cleaner, since no noxious HCl is evolved, as in the Leblanc process ;

(iv) the consumption of fuel is less, since there are no solutions to be evaporated as in Leblanc process ;

(v) the efficiency of the process is higher—the ammonia and carbon dioxide are recovered and used again.

The disadvantages of the process are (i) the whole of chlorine of the common salt is lost as calcium chloride, for which there is no adequate market yet ; (ii) the high cost of ammonia for replacing the losses.

Properties of sodium carbonate.—(i) Anhydrous sodium carbonate, called soda ash, is a white powder, which *melts* without decomposition at 852°, and absorbs moisture from air, forming the monohydrate, Na_2CO_3, H_2O.

(ii) It dissolves in water giving an alkaline solution owing to hydrolysis : $Na_2CO_3 + H_2O \leftrightharpoons NaOH + NaHCO_3$.

The aqueous solution on evaporation yields crystals of **washing soda,** $Na_2CO_3, 10H_2O$, which effloresce in air, giving **crystal-carbonate,** Na_2CO_3, H_2O.

(iii) The aqueous solution absorbs CO_2, yielding *sparingly soluble sodium bicarbonate*, which is filtered, washed dried and calcined at 250°—300° to give *pure sodium carbonate.*

$$Na_2CO_3 + H_2O + CO_2 \leftrightharpoons 2NaHCO_3.$$

Concentrated soda crystal, used in wool washing, is the sesquicarbonate, Na_2CO_3, $NaHCO_3$, $2H_2O$ (native *trona*). Sodium bicarbonate is used in medicine to reduce stomachic acidity and in baking powder.

(iv) It dissolves in dilute mineral acids with an effervescense of carbon dioxide : $Na_2CO_3+2HCl = 2NaCl+H_2O+CO_2$.

(v) It is causticised by lime to give caustic soda.

On being heated with ferric oxide, it yields sodium ferrite, which on treatment with hot water gives caustic soda. This is the principle of now-obsolete *Lowing process* :

$$Na_2CO_3 + Fe_2O_3 = 2NaFeO_2 + CO_2 \ ; \ 2NaFeO_2 + H_2O = 2NaOH + Fe_2O_3.$$

Uses of sodium carbonate.—It is used : (i) in the manufacture of glass, soap and caustic soda ; (ii) for washing textile fabrics ; (iii) in the softening of water ; (iv) for the preparation of other sodium salts ; and (v) as a reagent in the laboratory.

XIX

Compounds of Calcium

Calcium oxide, CaO, commonly called **quick lime,** or **lime** is made by decomposing limestone at a high temperature, about 1000° in a lime-kiln, which is a tall brick structure, generally built near a limestone quarry. $CaCO_3 \leftrightharpoons CaO+CO_2$—42,000 calories. Lumps of limestone are introduced into the kiln through a charging door at the top, and heated either by producer gas admitted at the base or by the combustion of coal (introduced along with limestone) inside the kiln. Lime works its way gradually down the kiln and is withdrawn at the base ; carbon dioxide passes out through an exit at the top (fig. 76).

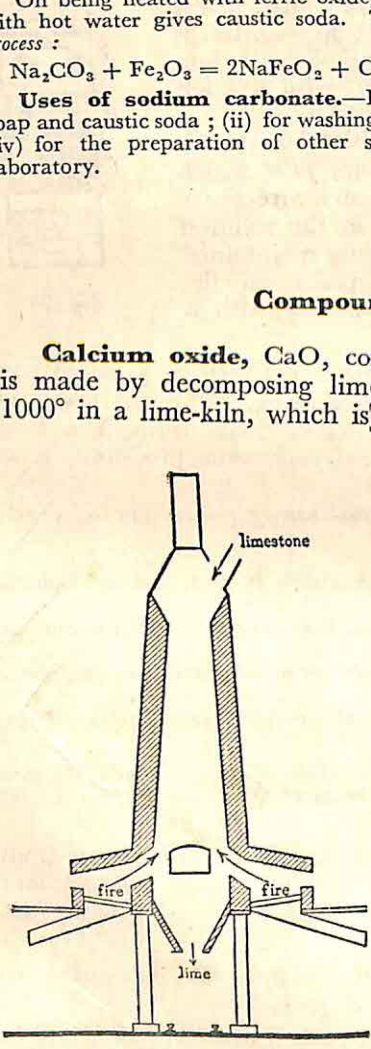


Fig. 76.

It is a white amorphous powder, which emits intense white light (*lime light*), when heated in the oxy-hydrogen flame. *It fuses* at 2570°. A basic oxide, it reacts wth acids and acidic oxides, yielding salts. It reacts with strongly heated silica, forming easily fusible calcium silicate ; $CaO+SiO_2 = CaSiO_3$.

It reacts with dry CO_2 only above 300°. It reacts with chlorine above 300° giving off oxygen :

$$2CaO+2Cl_2 = 2CaCl_2+O_2.$$

When quick lime is sprayed with water much heat is evolved and clouds of steam are given off ; lime combines with water, swells up, cracks and finally crumbles to a fine, dry, white powder of calcium hydroxide, $Ca(OH)_2$, called *slaked lime*,

$$CaO+H_2O=CaOH)_2.$$

The process is called *slaking of lime* and the product *slaked lime.*

Calcium hydroxide, slaked lime, $Ca(OH)_2$, is obtained by spraying water on the quick lime. It is sparingly soluble in water, about 0.23 gm. in 100 gms. of water at 0° : *it is less soluble in hot water than in cold.* The solution is called lime-water ; it readily absorbs carbon dioxide and is used as a test for the gas.

A suspension of slaked lime in water is called milk of lime. In its reactions it resembles caustic soda, and is largely used in industries as a cheap source of alkali.

Uses of lime.—Quick lime is used as a drying agent ; as a basic flux in metallurgy ; in the manufacture of calcium carbide ; and for producing lime light. Slaked lime is used for the manufacture of caustic soda and bleaching powder ; in glass-making and in the recovery of ammonia in the Solvay process ; or softening temporary hard water ; for the removal of hair from hides in leather industry ; for *whitewashing* of buildings ; for the purification of coal gas and sugar ; in agriculture ; in the manufacture of mortar and cement.

Mortar.—Builder's mortar is a mixture of slaked lime (1 part) and sand (3 parts) made into paste with water. It sets to a hard mass, by loss of water, into the bricks ; slaked lime is gradually converted to calcium carbonate by absorbing atmospheric carbon dioxide.

Soda lime is a dry mixture of slaked lime and caustic soda, made by slaking lime with strong caustic soda solution. It is used as a drying agent, as an absorbent for acid gases ; in *gas masks.*

Calcium sulphate, $CaSO_4$, occurs as *anhydrite*, $CaSO_4$, and as the dihydrate, $CaSO_4,2H_2O$, *gypsum, alabaster or satin-spar.* It is sparingly soluble in water, having the maximum solubility of 0.21% at 38°. When gypsum is heated, at about 120° it partially loses water, giving the hemi-hydrate, *plaster of Paris*, $2CaSO_4,H_2O$, which becomes anhydrous by heat at 200° ; slight decomposition into calcium oxide and sulphur trioxide occurs above 400°.

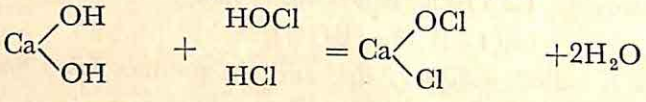
Plaster of Paris, $2CaSO_4,H_2O$.—It is made by heating gypsum at about 120°, without any contact with carbonaceous fuel (to prevent reduction into sulphide $CaSO_4+4C = CaS+4CO$), in large steel pots provided with mechanical stirrers or in a rotary kiln. Gypsum partially loses water producing plaster of Paris. The temperature is carefully controlled, since at higher temperature it is fully dehydrated, and is said to be *dead burnt*, as the product then loses its power of quick setting. Plaster of Paris, made into a paste with water, quickly sets to a hard mass, *with a slight expansion in the process* —setting being due to reconversion into gypsum.

$$\underset{\text{(gypsum)}}{2(CaSO_4,2H_2O)} \rightleftharpoons \underset{\text{(plaster of Paris)}}{2CaSO_4,H_2O}+3H_2O.$$

Plaster of Paris is used in taking casts in moulds ; in surgical bandages ; as a cement and wall plaster. Gypsum is used in the preparation of plaster of Paris and ammonium sulphate ; for filling or glazing paper ; as a fertiliser in agriculture ; in making *crayons*, so-called 'chalk' pencils.

Bleaching powder, Chloride of lime, *Ca(OCl)Cl*.—The most important derivative of hypochlorus acid is bleaching powder, calcium chloro-hypochlorite, Ca(OCl)Cl. This is obtained commercially by the action of chlorine upon slaked lime :

$$Cl_2 + H_2O = HCl + HOCl$$



$$\mathrm{Ca}\begin{matrix}\diagup \mathrm{OH}\\ \diagdown \mathrm{OH}\end{matrix} + \begin{matrix}\mathrm{HOCl}\\ \mathrm{HCl}\end{matrix} = \mathrm{Ca}\begin{matrix}\diagup \mathrm{OCl}\\ \diagdown \mathrm{Cl}\end{matrix} + 2H_2O$$

$$\overline{\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad}$$

$$Ca(OH)_2+Cl_2 = Ca(OCl)Cl+H_2O.$$

Chlorine gas (as obtained by the electrolytic process), free from moisture and carbon dioxide, and generally diluted with air, is passed into a series of lead chambers (typically ten) having concrete floors ; slaked lime (containing not more than 4 per cent moisture) is spread on the floor of the chambers to a depth of 3 inches, and this is then furrowed for uniform absorption of chlorine. The process is complete within a day's time, the chambers are *blown out with air* until the atmosphere is sweet, and also dusted with lime to remove the last trace of chlorine. The chambers are then opened and workmen get in and shovel the finished product through ports in the floor into barrels. The temperature is not allowed to rise above 35-40°C. The temperature is controlled by the circulation of cold water through cooling coils embedded in the floors. The product contains about 35-37% available chlorine.

In a continuous process, slaked lime is gradually pushed by mechanical rakes over and down the floors (typically ten) of a cylindrical tower of reinforced concrete and lined inside with tar and fire clay ; chlorine is fed in from the bottom. Chlorine is absorbed by slaked lime on counter-current principle.. The finished product is freed from chlorine by a blast of air at the bottom of the cylinder and then discharged into wooden drums. The temperature is controlled by circulating cold water through pipes embedded in the floors.

Bleaching powder is also called chloride of lime.

Properties.—(i) A white powder, smelling strongly of chlorine, bleaching powder absorbs moisture from the air, but is not deliquescent. It does not dissolve completely in water, always leaving a white residue of lime ; the aqueous suspension, however, contains the calcium hypochlorite in solution.

(ii) Unstable to heat ; the moisture and carbon dioxide of the atmosphere decompose it, liberating chlorine.

$$Ca(OCl)Cl+CO_2 = CaCO_3+Cl_2.$$

(ii) It reacts with dilute acids to give chlorine :

$$Ca(OCl)Cl+H_2SO_4 = CaSO_4+H_2O+Cl_2$$

$$Ca(OCl)Cl+2HCl = CaCl_2+H_2O+Cl_2.$$

The chlorine thus set free is known as available chlorine and is responsible for the *bleaching and oxidising properties* of bleaching powder. The valuation cf bleaching powder depends upon its content of available ehloirne which is expressed as the number of parts by weight of it which may be obtained from 100 parts by weight of the sample by treatment with dilute acids, and is generally spoken of as the "percentage of available chlorine" which is usually 35-37% in a commercial sample.

(iv) Cobalt salts decompose a suspension of bleaching powder catalytically, liberating oxygen : $2Ca(OCl)Cl = 2CaCl_2 + O_2$.

(v) A solution of sodium hypochlorite and chloride is formed by precipitating bleaching powder solution with sodium carbonate :

$$CaOCl_2 + Na_2CO_3 = CaCO_3 + NaOCl + NaCl.$$

(vi) It is a powerful oxidising agent ; thus it liberates iodine from an acidified solution of potassium iodide—a reaction made use of for its valuation :

$$Ca(OCl)Cl + 2KI + 2HCl = CaCl_2 + 2KCl + H_2O + I_2.$$

It oxidises sodium arsenite to arsenate—a reaction also used for its valuation.

$$Na_3AsO_3 + CaOCl_2 = Na_3AsO_4 + CaCl_2.$$

Uses.—Bleaching powder is used as a disinfectant, for sterilising water and in the manufacture of chloroform. But its principal use is for bleaching paper-pulp, cotton and linen.

The fabric to be bleached is boiled with dilute caustic soda to remove greasy impurities and then washed with water ; it is next steeped in a solution of bleaching powder and then left exposed to air for several hours when the bleaching is done by chlorine liberated from the bleaching powder by atmospheric carbon dioxide. The fabric is then washed with dilute sulphuric acid to destroy any excess bleaching powder, and finally with sodium sulphite solution to remove the last trace of chlorine.

Bleaching powder with a dilute acid is used for rendering wool unshrinkable.

Bleaching powder is now regarded as a mixture of calcium hypochlorite, $Ca(OCl)_2, 4H_2O$ and basic calcium chloride, $CaCl_2$, $Ca(OH)_2$, H_2O.

XX

Zinc At. wt. 65.38

Occurrence.—The principal ore of zinc is zinc sulphide or **zinc blende** ("black jack"), ZnS, which is usually associated with argentiferous *galena*. Less important minerals are : *calamine* (*smithsonite* in the U.S.A.), $ZnCO_3$; *electric calamine* (*calamine* in the U.S.A.), Zn_2SiO_4, H_2O ; *willemite* Zn_2SiO_4 ; *franklinite*, ZnO, Fe_2O_3 ; and *zincite* or red zinc ore, ZnO.

Extraction.—The most important source of zinc in zinc blende. The mixed ore of blende and galena is concentrated by oil-floatation process. The finely-crushed ore is churned up with water containing eucalyptus oil and a little acid—galena collects in the froth formed on the surface of the liquid, and is removed. The blende collects in a second froth produced by adding more oil and acid to the liquid—the gangue sinks to the bottom. Zinc is obtained from the zinc concentrate either (i) by the *reduction process*, or (ii) by the *electrolytic process*.

(i) **The reduction process.**—It consists of three steps : (a) *roasting*, (b) *smelting, and* (c) *refining* :

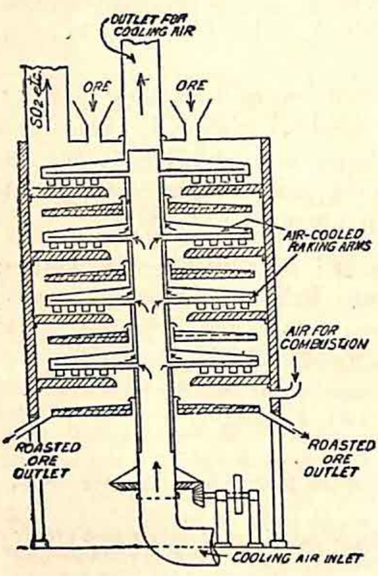


Fig. 77

(a) **Roasting.**—In order to convert the blende into zinc oxide, the zinc concentrate is roasted in air at a high temperature in a multiple-hearth roaster through which air circulates, and where the blende is raked in a series of shelves (fig. 77). Care is taken that only zinc oxide is produced, and no zinc sulphate, since it would again give sulphide in subsequent reduction. Some sulphate that is always formed is decomposed at the high temperature used.

$$2ZnS+3O_2 = 2ZnO+2SO_2 \,;$$
$$ZnS+2O_2 = ZnSO_4.$$

The sulphur dioxide may be utilised in making sulphuric acid. The carbonate ore, if used, is also calcined to eliminate carbon dioxide which readily oxidises zinc vapour :

$$ZnCO_3 = ZnO + CO_2 \,;$$
$$Zn + CO_2 \rightleftharpoons ZnO + CO.$$

(b) **Smelting.**—The roasted ore (zinc oxide) is then mixed with about half its weight of powdered coke, and packed into fire clay retorts R closed at one end and set in several rows in a furnace, sloping towards the open end (fig. 78)—the open end of each retort is fitted with a conical clay tube C (*condenser*) which in its turn is luted with clay with an iron tube P, known as the prolong. The furnace is heated to 1350° by producer gas and air *on the regenerative principle of heat economy*. The zinc oxide is reduced by coke, yielding carbon monoxide, and metallic zinc (b. pt. 920°) which distils off.

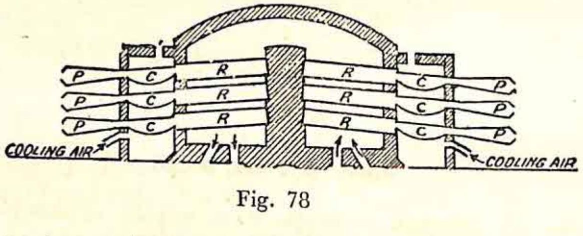


Fig. 78

$$ZnO + C = Zn + CO.$$

The zinc vapour passes with the carbon monoxide into the condensing system, where the zinc partly deposits as liquid metal in the condenser and partly as *zinc-dust* in the prolong. The carbon monoxide passes on and burns at the mouth of the condensers.

The first portion of the distillate, collecting as *zinc-dust* in the *prolong*, contains any *cadmium* that may be present in the ore, and some zinc oxide formed by the oxidation of zinc vapour by oxygen or carbon dioxide, initially contained in the condensing system. *Since zinc vapour is readily oxidised by carbon dioxide, the smelting is done in a carbon monoxide atmosphere.*

The molten metal in the condensers is transferred to moulds where it solidifies to give crude zinc, called **spelter,** which contains about 97 to 98 per cent zinc, 2 per cent lead, and traces of iron, cadmium and arsenic.

(c) **Refining.**—The crude zinc is refined by fractional distillation. The molten spelter is fed into a column heated above the boiling point of zinc (920°), when the zinc and cadmium distil out at the top and are condensed, and lead (b.p. 1620°) and iron (b.p. 2800°) collect at the bottom of the column. The molten zinc-cadmium alloy is then similarly treated in a second column heated above the b.p. of cadmium (767°) when the more volatile cadmium distils off at the top and very pure zinc (99.99 per cent) collects at the base of the column. Cadmium is recovered as a by-product.

(ii) **Electrolytic method.**—Pure zinc is made by electrolysis of an acidified solution of pure zinc sulphate with a high current density. The zinc concentrate is roasted in air below 700° to convert the blende into zinc sulphate. The roasted mass is leached with dilute sulphuric acid, when an impure solution of zinc sulphate is obtained. The solution is treated with milk of lime to precipitate iron and aluminium as hydroxides, and silica as calcium silicate, which are filtered off. The filtrate is then stirred with zinc-dust to precipitate the more noble metals copper and cadmium which are removed by filtration. The solution is next acidified and electrolysed with a lead anode and aluminium cathode—the zinc deposited on the cathode is stripped off ; it is of 99.95% purity.

Properties of zinc.—(i) Zinc is a bluish-white metal, which tarnishes in moist air by the formation of film of basic carbonate.

Though brittle below 100° and above 200°, commercial zinc is malleable and ductile between 100° and 150°, at which temperature it can be rolled into sheets and drawn into wire. Pure zinc is malleable at all temperatures.

Zinc burns in air with a green flame if strongly heated, forming white clouds of zinc oxide which settles in wooly flocks, *philosopher's wool*) : $2Zn+O_2 = 2ZnO$.

(ii) Pure zinc is not attacked by water ; commercial zinc, also zinc coated with copper, decomposes boiling water, giving off hydrogen. The red-hot metal reacts vigorously with steam, producing hydrogen. $H_2O+Zn = H_2+ZnO$.

(iii) Commercial zinc readily dissolves in HCl and dil. H_2SO_4 yielding hydrogen ; very pure zinc dissolves only exceedingly slowly. The metal is a convenient reducing agent in presence of dilute sulphuric acid : $Fe_2(SO_4)_3+Zn = ZnSO_4+2FeSO_4$.

Zinc dissolves in nitric acid. Zinc reacts with hot concentrated sulphuric acid, giving off SO_2 :

$$Zn+2H_2SO_4 = ZnSO_4+2H_2O+SO_2.$$

(iv) It dissolves in hot solutions of caustic soda and potash, yielding hydrogen and zincate. $Zn+2NaOH = Na_2ZnO_2+H_2$.

A mixture of zinc dust and caustic soda reduces an aqueous solution of a nitrate to ammonia.

$$NaNO_3 + 4Zn + 7NaOH = NH_3 + 4Na_2ZnO_2 + 2H_2O.$$

(v) It combines with chlorine if heated, yielding zinc chloride ; but it does not directly combine with hydrogen, nitrogen or carbon. Zinc nitride is formed by heating the metal in ammonia.

$$3Zn + 2NH_3 = Zn_3N_2 + 3H_2.$$

(vi) It precipitates the more noble metals, such as lead, copper, silver and gold, from their aqueous solutions.

$$CuSO_4 + Zn = ZnSO_4 + Cu.$$

Uses of zinc.—(i) Remarkably resistant to atmospheric corrosion, zinc is largely used to protect iron from rusting. The iron sheets or ware are cleaned by a sand-blast followed by 'pickling' with dilute hydrochloric acid, and then dipped in molten zinc containing a flux of ammonium chloride, when a thin adherent coating of zinc is formed ; the process is called galvanisation and the product *galvanized iron.* Iron articles may also be coated with zinc by heating them in zinc dust (sherardizing), by spraying, or by electro-deposition. Galvanised iron is not used for food containers, since zinc is poisonous.

(ii) Zinc is used for the manufacture of *zinc white,* and several useful alloys such as *brass* and *German-silver ;* for the precipitation of gold and silver in the cyanide method ; for the desilverisation of lead in Parkes process ; and as the anode material in galvanic cells.

(*ii*) Zinc dust or granulated zinc is an important reducing agent. *Zinc dust,* containing finely-divided zinc with some zinc oxide, is made by atomising molten zinc with a jet of high pressure air ; also found in the *prolong* during the smelting process. *Granulated zinc* having a large surface for a given weight, is prepared by pouring a thin stream of molten zinc in water.

Detection of zinc.—(i) Zinc compounds, on being heated with sodium carbonate on charcoal in blow pipe flame, yields a white incandescent residue (of zinc oxide) which is *yellow when hot,* and *white when cold.* The residue, on being moistened with cobalt nitrate and heated again, turns *green* (*Rinman's green*).

(ii) Ammonium sulphide yields with a solution of a zinc salt, a white precipitate of zinc sulphide insoluble in alkali and acetic acid, but soluble in dilute mineral acids.

(iii) Caustic soda gives with a solution of a zinc salt a white precipitate of zinc hydroxide, soluble in excess of the alkali.

XXI

Aluminium

Density 2.70, m.p. 659.8°C. b.p. 2270°. at. wt. 26.97.

Occurrence, etc.—Aluminium is not found native, but its compounds are widely distributed in nature. It occurs to the extent of 8% in earth's crust in many silicate rocks and clays. Important aluminium minerals are as :

(i) *silicates* : *felspar,* $K_2O.Al_2O_3.\ 6SiO_2$, and *kaolin* (china clay, $Al_2O_3,\ 2SiO_2.\ 2H_2O$; also *micas, garnet* and *tourmaline.*

(ii) *oxides* : The oxide Al_2O_3 is found anhydrous as *corundum* and *emery* or hydrated as *diaspore,* $Al_2O_3.H_2O$; *bauxite,* $Al_2O_3.2H_2O$; *gibbsite,* $Al_2O_3.\ 3H_2O$. The precious stones valued as gems, *e.g., ruby* (red), *amethyst* (violet), *sapphire* (blue), *topaz* (yellow), and *emerald* (green), consist of aluminium oxide coloured by traces of oxides of Fe, Co, Cr, Mn and Ti.

(iii) *fluoride* : *cryolite,* $AlF_3.\ 3NaF$; it is found in Greenland only.

(iv) *phosphate* : *turquoise,* $AlPO_4.\ Al(OH)_3.\ H_2O$, coloured blue by the presence of copper phosphate.

Other minerals are *spinel,* $MgO.Al_2O_3$; *chrysoberyl,* $BeO.Al_2O_3$; *alunite,* $K_2SO_4.Al_2(SO_4)_3.4Al(OH)_3$.

Clay is formed by the disintegration of *ortho clase or* (*potash*) *felspar* which is a constituent of granite rocks, due to the weathering action of water and carbon dioxide.

$$K_2O.\ Al_2O_3.\ 6SiO_2+2H_2O+CO_2 = K_2CO_3+Al_2O_3.\ 2SiO_2.\ 2H_2O+4SiO_2.$$

Pure clay or kaolin (china clay) is white and consists of hydrated aluminium silicate, $Al_2O_3.\ 2SiO_2.\ 2H_2O$, but most clays are coloured due to presence of ferric oxide and other impurities.

Aluminium is manufactured from bauxite, $Al_2O_3,\ 2H_2O$. No cheap method is available to extract the metal from caly. Analysis of few samples of Indian bauxite :

Source	SiO_2	TiO_2	Al_2O_3	Fe_2O_3	H_2O
Katni	1.2	8.8	60.2	2.6	25.4
Ranchi	0.3	7.4	66.9	5.9	21.4

Extraction.—Aluminium was first isolated is 1827 by Wohler by the action of potassium upon aluminium chloride. Aluminium was formerly obtained by converting alumina into chloride by heating with charcoal in chlorine, and then reducing sodium aluminium chloride with sodium :

$$Al_2O_3 + 3C + 3Cl_2 = 2AlCl_3 + 3CO\ ;\ NaAlCl_4 + 3Na = 4NaCl + Al.$$

The metal is now exclusively obtained from *bauxite* by an electrolytic process simultaneously discovered in 1886 by Hall in America and Heroult in France.

Crude bauxite contains the impurities *iron oxide and silica* which must be removed before electrolysis, otherwise the resulting aluminium contains iron and silicon, and is readily corroded by water. Hence the manufacture of aluminium consists of two steps : (i) *purification of the bauxite*, and (b) *electrolysis of purified bauxite.*

(a) **Purification of the bauxite : Bayer's process.**—The calcined bauxite is finely ground, and then digested with a strong (sp. gr. 1.45) solution of caustic soda in an autoclave under 80 lbs. pressure at 150° for 2 to 8 hours when aluminium oxide goes into solution as sodium aluminate, the iron oxide remaining undissolved. When the digestion is complete, the hot sodium aluminate solution is filtered from the insoluble oxide of iron and other impurities (*red mud*). The solution is then diluted, slowly cooled and agitated for several hours with freshly precipitated hydrated alumina, when the sodium aluminate undergoes hydrolysis and hydrated alumina (β-alumina) is precipitated. The precipitate is filtered, washed and cacined to pure alumina (99.55 per cent) in a rotary kiln at 1100°C.

$$Al_2O_3+2NaOH = 2NaAlO_2+H_2O\ ;$$
$$2NaAlO_2+4H_2O \rightleftharpoons 2Al(OH)_3+2NaOH\ ;$$
$$2Al(OH)_3 = Al_2O_3+3H_2O.$$

The filtrate contains caustic soda ; it is concentrated by evaporation and used again for digestion of a fresh charge.

Bauxite with high silica content cannot be treated by Bayer's process, since much aluminium is lost due to the formation of insoluble sodium aluminium silicate. Bayer's process is best adapted to bauxite containing 55 to 60% Al_2O_3, and relatively low in silica (below 7% SiO_2) content.

In the old process the bauxite is heated to bright redness with sodium carbonate, and the mass is readily lixiviated with water—the resulting sodium alminate and sodium silicate dissolve, ferric oxide remaining insoluble, Aluminium hydroxide is precipitated from the solution by carbon dioxide at 50° to 60°, and is ignited to the oxide. $Al_2O_3 + Na_2CO_3 = 2NaAlO_2 + CO_2$;

$$2NaAlO_2 + 3H_2O + CO_2 = Na_2CO_3 + 2Al(OH)_3$$

Bauxite may also be purified by heating with coke at 1800° in a current of nitrogen (obsolete **Serpek's process**)—the resulting aluminium nitride being decomposed by hot water, yielding ammonia and aluminium hydroxide which is ignited to the alumina.

$$Al_2O_3 + 3C + N_2 = 2AlN + 3CO \; ; \; AlN + 3HOH = NH_3 + Al(OH)_3$$

(b) **Electrolysis of alumina.**—Aluminium is obtained by the electrolysis of the pure alumina (20 parts) dissolved in a bath of fused cryolite (60 parts) and fluorspar (20 parts)—the melt is kept at 950°C, the passage of current supplying sufficient heat to maintain the required temperature. The electrolysis is carried out in an iron tank (fig. 79) lined with blocks of carbon which forms the cathode—the anode is a set of hard carbon (low-ash petroleum coke) rods A suspended in the tank from copper clamps. During electrolysis aluminium (m.p. 659°) is liberated at the cathode and collects in the liquid state on the floor of the cell whence it is tapped out ; oxygen is evolved at the anode which is burnt away to carbon monoxide—hence the charge is covered with a layer of coke to minimise the oxidation of the expensive anodes.

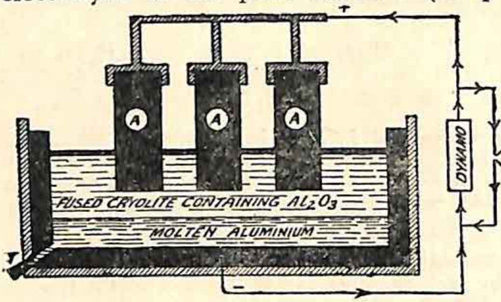


Fig. 79

$$Al_2O_3 \leftrightharpoons 2Al^{+++} + 3O''$$

$$2Al^{+++} + 6e = 2Al \text{ (at cathode) } ; \; 3O'' = 3O \text{ (at anode) } + 6e$$

Fresh alumina is added at intervals to supply that decomposed. When the supply of alumina in the bath gets exhausted the voltage suddenly jumps from 5 to 6 volts up to 40 to 60 volts (this is known as the *anode effect*), there being an increase in the resistance of the bath. When the anode effect occurs an electric lamp connected across the terminals of the cell which normally glows dimly, becomes very bright. This acts as a signal for the supply of fresh alumina into the bath. The voltage used is 5-6 volts and the energy consumption is 10 K.W.H. per lb.

Cryolite acts as a flux in the process—its only source is Greenland. Synthetic cryolite, free from silica, is made for use in the aluminium extraction by the reaction.

$$AlF_3 + 3NH_4F + 3NaNO_3$$
$$= AlF_3, 3NaF + 3NH_4NO_3$$

(c) **Refining**—The aluminium produced has a purity of 99%, its chief impurities being iron and silicon. The metal is refined electrolytically by Hoope's process. The electrolytic cell contains three liquid layers of different densities. Pure molten alumi-cathode at the top, liquid crude

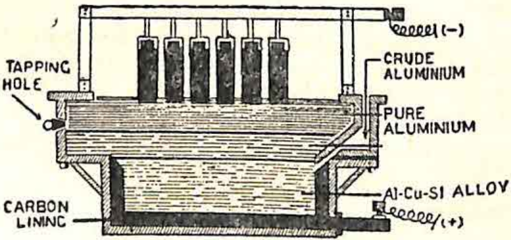


Fig. 80

aluminium-copper alloy anode at the bottom, with a layer of molten mixture of cryolite, aluminium fluoride, barium fluoride and alumina electrolyte in between (fig. 80). In course of electrolysis aluminium dissolves out from the anode, and is deposited at the cathode—the refined Al has a purity of 99.99%.

Properties of aluminium.—(i) Aluminium is an extremely light (density 2.70), silver-white metal, sufficiently malleable and ductile to be rolled into foil or drawn into wire. It has a high tensile strength and a good thermal and electrical conductivity.

(ii) It is coated with a protective film of aluminium oxide when exposed to air, and hence does not readily tarnish in air.

But corrosion occurs if the film is broken by amalgamation with mercury (by rubbing the surface with mercury or mercuric chloride).

(iii) Aluminium is not attacked by pure water owing to the protective oxide film on the surface ; sea water or saline solutions readily attack it. Amalgamated aluminium decomposes water even in the cold. $2Al+6HOH = 2Al(OH)_3+3H_2$.

(iv) It readily dissolves in hydrochloric acid. But it is scarecely attacked at all either by dilute sulphuric acid or by dilute or concentrated nitric acid. Hot concentrated sulphuric acid dissolves aluminium yielding sulphur dioxide.

$$2Al+6HCl = 2AlCl_3+3H_2 ;$$
$$2Al+6H_2SO_4 = Al_2(SO_4)_3+3SO_2+6H_2O.$$

Aluminium is corroded by organic acids, most rapidly when the acid is diluted or anhydrous.

(vi) It combines directly, when heated with nitrogen, chlorine, sulphur, and carbon, forming the nitride AlN, chloride, $AlCl_3$, sulphide, Al_2S_3, and carbide, Al_4C_3, respectively.

(v) It readily dissolves in hot caustic soda or potash solution, forming aluminate :

$$2Al+2NaOH+2H_2O = 2NaAlO_2+3H_2.$$

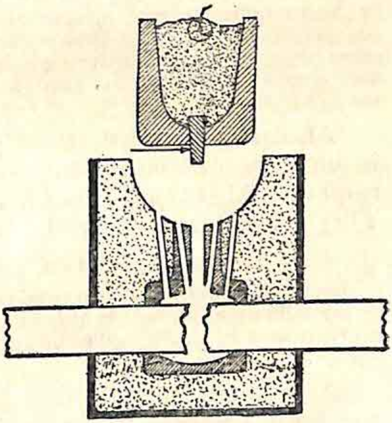


Fig. 81

(vii) Aluminium has a strong affinity for oxygen at and above 1000°, and the great evolution of heat resulting from its combination with oxygen is utilised in Goldschmidt's **thermit** or **alumnino-thermic process** for reducing metallic oxides (e.g., MnO_2 and Cr_2O_3) and for the preparation of molten metals *in situ*, e.g., molten iron for welding rails and machine parts. *Thermite* is a mixture of aluminium powder and iron oxide. A mixture of aluminium filings (1 part) and iron oxide (3 parts) is ignited in a crucible by a fuse of magnesium, when a violent reaction occurs, producing molten iron at a temperature of about 2500°. The liquid iron is tapped from below directly on to the joint to be welded (fig. 81).

$$Fe_2O_3+2Al = 2Fe+Al_2O_3+199{,}000 \text{ calories}.$$

Uses of aluminium.—(i) On account of its *lightness* and fair *tensile strength*, aluminium is used in making body of air-ships and motor cars ; for the same reasons it is used for making alloys.

Alloy	Composition	Uses
(i) Magnalium	Al 98 Mg 2	Cheap balance, machined articles—the alloy can be worked on lathe.
(ii) Duralumin Y-alloy	Al 95 Cu 4 Mg 0.5 Mn 0.5 Al 92.5 Cu 4 Mg 1.5 Ni 2	Construction for aircrafts—the alloys are light, tough and resist corrosion.
(iii) Aluminium bronze	Al 10 Cu 90	Coins, utensils, photoframes.
(iv) Alclad	Duralumin covered with a thin coating of Al	For making sea planes—the alloy resists corrosion by sea water.
(v) Alnico	Steel 50 Al 20 Ni 20 Co 10	For making permanent magnets.

(ii) On account of its good electrical conductivity (60% of that of an equal volume of copper, or 200% of that of a copper conductor of equal weight) it finds use in transmission wires. (iii) On account of its good thermal conductivity, it is used in making *cooking utensils*. (iv) Since it resists corrosion it is used as *aluminium paint—aluminium* powder, produced by stamping thin aluminium sheet in oil, is used as the paint. Aluminium foils are used in wrapping cigarettes, etc. (v) Due to its great affinity for oxygen, aluminium is used in *thermite*—utilised in welding rails and machine parts, in incendiary bombs, and in the preparation of chromium and manganese and also as a reducing agent. Ammonal, a mixture of ammonium nitrate and aluminium powder, is used in explosive bombs. Aluminium powder finds use in fire-works.

Aluminium sulphate, $Al_2(SO_4)_3$, is made by dissolving alumina in hot concentrated sulphuric acid ; ill-defined crystals of aluminium sulphate, $Al_2(SO_4)_3$, $18H_2O$, are deposited on cooling the solution. They are recrystallised from water containing alcohol.

$$Al_2O_3+3H_2SO_4 = Al_2(SO_4)_3+3H_2O.$$

Crude aluminium sulphate containing ferric sulphate (which cannot be separated by crystallisation) is made by digesting bauxite with 62% sulphuric acid—the solution is evaporated to a solid, called **alumino-ferric** largely used in purifying water and sewage.

Aluminium sulphate may however, be crystallised after reducing the ferric sulphate to the ferrous state by sodium sulphide.

Crude aluminium sulphate is also made by digesting china clay (kaolin) with concentrated sulphuric acid.

$$Al_2O_3,\ 2SiO_2,\ 2H_2O \text{ (kaolin)} + 3H_2SO_4 = Al_2(SO_4)_3 + 2SiO_2 + 5H_2O.$$

A colourless, crystalline solid, it is soluble in water—the solution is acid due to hydrolysis.

$$Al_2(SO_4)_3+6H_2O \leftrightharpoons 2Al(OH)_3+3H_2SO_4$$

It forms an important series of double salts, known as alums. The hydrate forms the anhydrous salt on gentle heating, but at a red heat it decomposes into alumina, sulphur dioxide, and oxygen.

$$2Al_2(SO_4)_3 = 2Al_2O_3+6SO_2+3O_2.$$

It is used as a mordant in dyeing and calico-printing ; in the sizing of paper ; in purifying sewage and water ; in 'foam' fire extinguishers ; in tanning kid leather.

Alums.—The name alum was given originally to the double-salt, potassium aluminium sulphate, K_2SO_4, $Al_2(SO_4)_3$, $24H_2O$. But the name *alum* is now given to all double salts of the type M_2SO_4, $R_2(SO_4)_3$, $24H_2O$, where M is a monovalent metal and R a trivalent metal. M may be Na, K, Rb, Cs or NH_4 ; R may be Fe, Al, Cr, Mn, or Co. The alums are isomorphous and form octahedral crystals. Examples are :

Potash or common alum ...	K_2SO_4, $Al_2(SO_4)_3$, $24H_2O$.
Ferric ammonium alum ...	$(NH_4)_2SO_4$, $Fe_2(SO_4)_3$, $24H_2O$.
Chrome alum	K_2SO_4, $Cr_2(SO_4)_3$, $24H_2O$.
Ammonia alum	$(NH_4)_2SO_4$, $Al_2(SO_4)_3$, $24H_2O$.

Potash alum, $K_2SO_4,Al_2(SO_4)_3,24H_2O$, deposits in colourless octahedral crystals when a hot solution containing equimolecular quantities of potassium and aluminium sulphates is set aside to crystallise.

Alum is made commercially from : (i) **Bauxite**—Bauxite is ground to powder and then digested at steam heat with 62 per cent sulphuric acid in a lead-lined steel tank fitted with steam coils and then treated with barium sulphide to reduce the ferric sulphate to the ferrous state—the clear aluminium sulphate solution is either decanted or filtered, after settling, and then mixed with the correct amount of potassium sulphate. The mixed solution on concentration and cooling yields alum crystals. It may be purified by recrystallisation and obtained completely free from iron.

$$Al_2O_3+3H_2SO_4 = Al_2(SO_4)_3+3H_2O.$$

(ii) **Alunite** or **alum stone,** $K_2SO_4,Al_2(SO_4)_3,4Al(OH)_3$—the alunite is calcined and then digested with sulphuric acid to convert the alumina to aluminium sulphate. Required amount of potassium sulphate is then added to the solution and the alum is allowed to crystallise.

Formerly alum was obtained by simply calcining alunite in air, leaching with water, and crystallising—as so made it is called **Roman alum.**

(iii) **Alum shale** which is aluminium silicate containing iron pyrites, FeS_2. The shale is roasted in heaps, when the oxidation of the pyrites gives ferrous sulphate and sulphuric acid, which converts aluminium silicate to aluminium sulphate. The roasted mass is extracted with water ; requisite quantity of potassium chloride is added to the extract and the solution is crystallised for alum.

Potash alum forms colourless octahedral crystals having an astringent taste. It dissolves in water, and melts at 92°. It loses all its water of crystallisation at 200°, leaving a residue of anhydrous sulphate, known as *burnt alum*.

Alum is used as 'styptic' to stop bleeding from small cuts. Alum is put to the same uses as aluminium sulphate (*vide supra*).

Detection of aluminium.—(i) Aluminium compounds, mixed with sodium carbonate and heated on charcoal in a blow pipe flame, yields a *white incandescent mass*, which on being moistened with cobalt nitrate and heated again, turns *blue*

(Thenard's blue). (ii) Ammonium hydroxide, when added to a solution of an aluminium salt, gives a white gelatinous precipitated of aluminium hydroxide, even in presence of ammonium chloride ; the precipitate dissolves in caustic soda or potash forming aluminate, and is reprecipitated by heating with ammonium chloride :

$$NaAlO_2 + NH_4Cl + H_2O = Al(OH)_3 + NH_3 + NaCl$$

Copper sulphate, blue vitriol, $CuSO_4,5H_2O$.—Blue vitriol is made (i) by spraying dilute sulphuric acid on to scrap copper packed in a lead-lined tower up which a current of air is sent ; copper dissolves in presence of air ; forming copper sulphate :

$$2Cu+2H_2SO_4+O_2 = 2CuSO_4+2H_2O.$$

The solution is circulated by means of a pump until sufficiently concentrated and then left for crystallisation in a vat, when crystals of blue vitriol deposit.

(ii) by heating scrap copper with sulphur, and then roasting the mass in air in order to convert the resulting sulphide to sulphate, which is finally leached with dilute sulphuric acid and crystallised.

$$Cu + S = CuS \ ; \qquad CuS + 2O_2 = CuSO_4.$$

(iii) by the 'weathering' of copper pyrites which is first gently roasted to convert copper sulphide to sulphate ; copper sulphate is leached out with water and crystallised.

Commercial copper sulphate contains isomorphous ferrous sulphate. It is purified by recrystallisation from water containing a little nitric acid, when the ferrous sulphate is oxidised to ferric sulphate which, not being isomorphous with copper sulphate, remains in solution.

On exposure to air the blue pentahydrate effloresces to give the trihydrate, and when heated at 100° it losses four molecules of water and forms the monohydrate, $CuSO_4,H_2O$; at about 250° it yields the colourless anhydrous salt, which rapidly absorbs moisture to give the blue pentahydrate, and *hence its use for detecting traces of water in gases and non-aqueous liquids.* Copper sulphate it completely decomposed at 750°, leaving a residue of cupric oxide.

Copper sulphate readily absorbs hydrogen chloride : $CuSO_4 + 2HCl = CuCl_2 + H_2SO_4$; the reaction may be used for removing HCl from other gases, such as sulphur dioxide.

Copper sulphate is toxic to lower organisms, and hence its use as a germicide and fungicide in agriculture, e.g., vines and potatoes are sprayed with Bordeaux mixture (a solution of copper sulphate mixed with slaked lime). It is also used in copper plating, in dyeing and calicoprinting, and for preserving wood and hides.

Copper sulphate reacts with potassium iodide solution, giving a *white pdecipitate of cuprous iodide*, CuI, and quantitatively liberating iodine ; the reaction is used in estimating copper :

$$2CuSO_4+4KI = 2K_2SO_4+2CuI+I_2.$$

Copper sulphate reacts with potassium cyanide giving a white precipitate of cuprous cyanide and evolving cyanogen gas—the cuprous cyanide dissolves in excess of KCN forming stable potassium cuprocyanide, $K_3[Cu(CN)_4]$.

$$2CuSO_4+4KCN = 2CuCN+(CN)_2+2K_2SO_4 \ ;$$
$$CuCN+3KCN = K_3[Cu(CN)_4]$$

XXII

Iron

Density 7.86, m.p. 1539°C, b.p. 2450°C, atomic weight 55.85.

History.—Because of its manifold applications, iron is by far the most important metal. It came into general use at a very early date in human history, and gradually displaced bronze, which was in use as early as 3000 B.C. The famous iron pillar at Delhi, remarkable for its freedom from rust, which was probably built about 300 A.D., bears testimony to the fact that iron smelting reached a high level of perfection in ancient India.

Occurrence.—Native iron is rarely found, except in meteorites—the most notable deposit being at Disco Island, Greenland. The most important ores of iron are : **red hæmatite,** Fe_2O_3 ; **brown hæmatite** *or* **limonite** $2Fe_2O_3$, $3H_2O$; **magnetite,** Fe_3O_4 ; and *spathose* or **spathic iron ore** or *siderite,* $FeCO_3$. *Iron pyrites,* FeS_2 is important as a source of sulphur—burnt pyrites, chiefly ferric oxide, may be smelted for iron

Huge deposits of iron ores, chiefly hœmatite, are found in Maurbhunja, Keonjhur, Singhbhum, Mysore, and elsewhere in India. Principal iron producing centres in India are Jamshedpur in Bihar, Kulti and Burnpur in West Bengal, and Bhadrabarti in Mysore. Huge iron smelting projects have recently been started at Rourkella (Orissa), Vilai (M. P.) and Durgapur (West Bengal). The Indian hœmatite ores contain 60 to 65 per cent of iron on an average.

Metallurgy.—The iron ores which contain much sulphur, phosphorus and arsenic are not suitable as source of the metal as these impurities would render it brittle and unworkable. Iron is extracted from its oxide and carbonate ores only (burnt pyrites which is chiefly ferric oxide, is sometimes used) by reduction with carbon in a blast furnace. The process is carried out in two steps :

(i) **Preliminary roasting or calcination.**—The ore is burnt

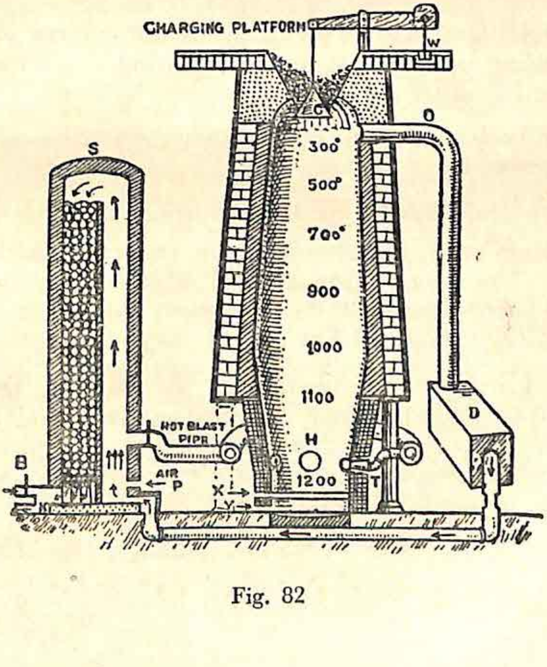


Fig. 82

with a little coal in heaps or in shallow kilns in order to drive off most of the moisture, carbon dioxide, sulphur and aresenic ; ferrous oxide is converted to ferric oxide to avoid the formation of ferrous silicate in the slag during smelting. The ore is also rendered porous. The roasted mass contains ferric oxide, Fe_2O_3.

(ii) **Smelting or reduction in the blast furnace.**—The roasted ore is mixed with *coke* and *limestone* (flux) and charged into the blast furnace (fig. 82), where the ferric oxide is reduced to iron.

The **blast furnace** is a cylindrical, vertically placed shaft made of steel plates lined internally with refractory firebricks, and about 50—100 ft. in height and 15—20 ft. in diameter. The furnace broadens slightly from the top downwards, reaching the broadest point (about two-thirds of the way to the ground) at the *boshes*, and then narrows gradually to a **hearth** (about 10 ft. in diameter and the same height) at the base. The hearth is provided with two plug holes, stopped with clay, for letting out the molten slag and iron respectively, the *slag hole* is at a rather higher level than the tapping hole for iron. A little above these plugs the hearth is pierced with a set of holes, called **tuyeres.** The mouth is closed with a **cup and cone** device meant for introducing the charge into the furnace.

The furnace is started by burning piles of wood inside, and a mixture of roasted ore, hard coke, and limestone is intermittently fed into the furnace by means of the cup and cone device—the charge consists of 1 ton of coke and 10 cwt. of limestone to $2\frac{1}{2}$ tons of ore, which produce 1 ton of cast iron. A blast of dry (by passing over silica gel) air, preheated to about 800°C, is forced into the base of the furnance through the tuyeres. The coke burns in the air blast to carbon monoxide and raises the temperature to about 1500°C. $2C+O_2=2CO$. The temperature of the furnace increases continually from the mouth (400°) to the hearth (1500°).

The descending charge of solids meets the current of hot carbon monoxide passing upwards when the following reactions take place, leading to the formation of iron.

Above the boshes at abou 600°—900°, the ferric oxide is reduced by carbon monoxide to spongy iron.

$$Fe_2O_3+3CO \leftrightharpoons 2Fe+3CO_2.$$

But the reaction being *reversible*, the reduction is not complete at this stage. The spongy iron absorbs sulphur from the fuel. The limestone in the charge is decomposed into lime and carbon dioxide. $CaCO_3 \leftrightharpoons CaO+CO_2$.

Near the centre of the furnace at about 900°, the reaction : $2CO \leftrightharpoons CO_2+C$ deposits finely divided carbon which completes the reduction $Fe_2O_3+3C \leftrightharpoons 2Fe+3CO$. The phosphates and the managanese compounds in the ore, and also a part of silica are reduced to phosphorus, manganese and silicon which readily alloy with iron.

$$Ca_3(PO_4)_2+3SiO_2+5C=3CaSiO_3+2P+5CO.$$

$$SiO_2+2C=Si+2CO\ ;\ \ Mn_2O_3+3C=2Mn+3CO$$

The remainder of the silica (the gangue in the ore) combines with lime to form a fusible *slag of calcium silicate :*

$$CaO + SiO_2 = CaSiO_3.$$

At the hearth of the furnace at about 1500°, the iron containing carbon, sulphur, phosphorus, manganese, and silicon, fuses—the slag floats on the surface of molten iron and thereby prevents its oxidation by the air blast. The molten slag runs out from above the molten iron. The molten iron is tapped out at intervals into sand moulds to form **pig iron** (or cast iron), or is sent in the molten state to steel furnaces. The molten iron is directly cast into V-shaped bars called *pigs*. **Cast iron** is re-melted pig iron.

The hot exhaust gases, leaving the furnace by an outlet at the top, and having the composition—nitrogen 60, CO 24, CO_2 12, CH_4 and H_2 4 by volume are utilised in preheating the air blast in Cowper stoves on a regenerative principle. The blast furnace operates day and night for years until its lining wears out.

The slag finds applications in the reclamation of land ; for road making ; in the manufacture of 'slag wool' and cement.

Varieties of iron.—Three varieties of commercial iron are *cast iron, wrought iron* and *steel*.

Cast iron (pig iron).—It contains 2.2 to 4.5 per cent of carbon, together with silicon (0.5 to 2 per cent.), manganese (0.2 to 1 per cent.), phosphorus (0.7 per cent.), and sulphur (0.3 to 1 per cent.) in small amounts. Carbon may be present in the free state as *graphite* or in combination as iron carbide, Fe_3C (cementite). Cast iron melts at 1200°, and is very hard and brittle, and hence is of little value for structural purposes.

It finds uses in making castings which are not subjected to violent shocks e.g., fire grates, lamp-posts, railings, pipes, parts of machinery, etc. About three quarters of the total output of cast iron is made into steel and a small quantity into wrought iron.

Wrought iron.—*Malleable* or *wrought* iron is very nearly pure iron, containing only 0.12 to 0.25 per cent of carbon, and melts at a higher temperature (1400° to 1500°) than cast iron.

It is made by oxidising away the carbon and other impurities in cast iron by melting the latter on the bed of a reverberatory furnace, lined with hœmatite, Fe_2O_3.

Soft and malleable, it can be easily welded and worked by hammering, and hence its use by the blacksmiths. Fibrous in structure, it has a high tensile strength. It finds uses in making chains, wire anchors, and cores of electromagnets.

Steel.—Steel is an alloy of iron with a carbon content of 0.15 (mild steel) to 1.5 per cent (hard steel). It may be made (i) from cast iron, (ii) from wrought iron.

Steel from cast iron.—Steel is produced from cast iron by first *removing the impurities* in cast iron, e.g., C, Si, Mn, S, and P, by oxidation, and then adding the correct *amount of carbon* according to the quality of steel desired.

The operation is carried out by Bessemer process or the *Siemens-Martin* open-hearth process. There are two modifications of each process : (i) the **acid process** for the treatment of cast iron which is free from phosphorus—the converter or the hearth is lined with *silica bricks* in the acid process : (i) the **basic process** for the treatment of cast iron containing phosphorus—in the basic process the converter or the hearth is given a lining with *calcined dolomite* or *magnesite.* Iron containing phosphorus cannot be treated by the acid process, *since an interaction between the phosphatic slag and silica lining would occur.*

The Bessemer process (1855).—The process is carried out in a converter (fig. 83) which is a large pear-shaped iron vessel (holding 10 tons of metal) with a perforated bottom through which a blast of air can be forced in fine jets. It is supported on two horizontal arms (trunnions) so that it can be tilted in a vertical plane. The converter is lined with refractory silica bricks (*acid lining*) or with magnesia and lime (*basic lining.*)

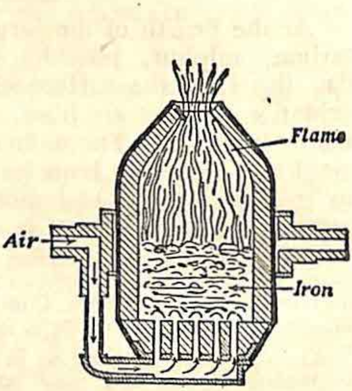


Fig. 83

The acid Bessemer process is used to treat cast iron which is free from phosphorus. The converter is tilted in a horizontal position and the charge of molten cast iron is run in through the mouth. The blast of air is then turned on, and the converter is swang into the vertical position.

Air rises through the molten metal in small bubbles and rapidly brings about the oxidation of the impurities—the heat of oxidation keeps the metal in the molten state. Silicon and manganese are first oxidised and pass into the *slag* as managanese silicate. $2Mn+O_2 = 2MnO$; $Si+O_2 = SiO_2$; $MnO+SiO_2 = MnSiO_3$. Carbon is then oxidised to carbon monoxide which *burns* at the mouth of the converter with an *orange-yellow flame* edged with blue. After 6 to 8 minutes the flame drops indicating that the carbon has been removed.

$$2C+O_2 = 2CO \; ; \; 2CO+O_2 = 2CO_2.$$

The converter is again tilted, the blast stopped, and a charge of requisite amount of **spiegeleisen** (an alloy of iron, manganese and carbon) added to the molten iron for *deoxidation* and *recarburisation*—the blast is continued just for a few moments to bring about a thorough mixing. C and Mn act as *deoxidisers* in the first instance and reduce any oxide of iron that is present—the excess dissolves in the molten iron to form steel. The molten steel is then poured into ladles by tilting the converter, separated from the slag floating on the top, and run into moulds.

Sometimes *a little Al* or *ferro-silicon* is added to molten steel to avoid blow holes in the castings due to bubbles of gas which react with the added elements.

The basic Bessemer or **the Thomas-Gilchrist process** used to treat cast iron containing phosphorus. A charge of *limestone* and coke is first introduced into the converter and the blast of air turned on. The molten cast iron is then run in and the blast continued.

Silicon and manganese are at first oxidised and pass into the slag; then carbon and phosphorus are oxidised simultaneously; carbon monoxide burns at the mouth of the converter. The air blast is continued after the carbon monoxide flame sinks for the completion of the oxidation of phosphorus. The phosphorus pentoxide reacts with lime and forms a slag containing calcium phosphate and free lime (basic slag).

$$4P+5O_2 = 2P_2O_5\ ;\ 4CaO+P_2O_5 = Ca_3(PO_4)_2,\ CaO.$$

The molten iron is poured out into a ladle, *separated from the slag*, (the basic slag must be removed before spiegeleisen is added, as otherwise the phosphorus would again pass back into iron), and *then* mixed with a charge of requisite amount of *spiegeleisen* for *recarburisation* and *deoxidation*, to form the steel. The basic Bessemer slag, also called **Thomas slag,** contains calcium phosphate and is used as a fertiliser.

The open hearth process (1863-64).—Most of the high grade steels are now made by the open-hearth furnace (fig. 84). Molten cast iron is run on the hearth which is lined with silica in the acid process (if the iron is free from phosphorus) or with lime and magnesia in the basic process (if phosphorus is present). *Scrap steel and oxide ore* of iron (hœmatite) are added to the charge of cast iron; limestone is also added if the iron contains phosphorus. The charge is melted by heating the furnace regeneratively with producer gas—the air and producer gas are injected through separate regenerators of chequer brick work used in pairs and alternately crossed by the hot exhaust gases and the fuel gases.

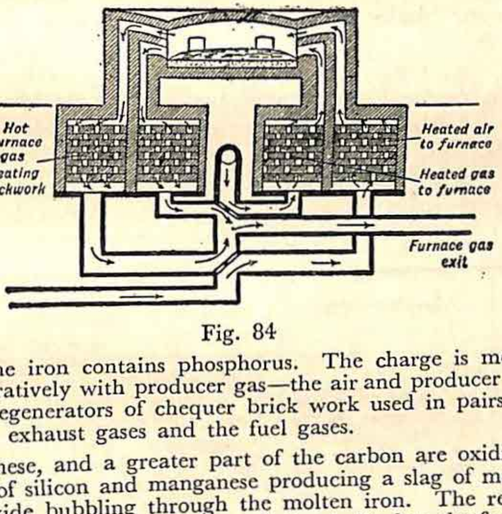


Fig. 84

Silicon, manganese, and a greater part of the carbon are oxidised by the iron oxide—the oxides of silicon and manganese producing a slag of manganese silicate and carbon monoxide bubbling through the molten iron. The remaining carbon and phosphorus are oxidised by the excess of air admitted to the furnace—the oxide of phosphorus forming a slag of calcium phosphate, as in Bessemer process.

The molten iron is then poured out into ladles, separated, from the slag and a charge of *spiegeleisen* is added, after the removal of the slag, for deoxidation and recarburisation. A little Al or ferro-silicon is added to the finished steel to avoid blow holes in castings.

The open hearth process offers several advantages over the Bessemer process: (i) The composition of the product can be accurately followed and controlled, all the impurities including phosphorus being *completely* eliminated, and hence high grade steels are produced. Phosphorus is only *incompletely* removed by the Bessemer process. (ii) Scrap iron and oxide ore can be utilised; the open-hearth process calls for a good deal of steel scrap. (iii) Cast iron from low grade ores can be used.

The open hearth operation lasts 8-10 *hours* and requires the use of fuel gases, whereas the Bessemer process is complete within 8-10 minutes and needs no fuel. About 80% of the total output of steel is made by the open hearth process.

A combination of the acid Bessemer and the basic open hearth processes is often practised for the treatment of phosphatic pig iron, and is known as the **Duplex process.** Electric furnaces are used for making special high quality steel by refining the Bessemer or open hearth steel.

Properties of steel.—The properties of steel depend on the content of carbon and on the heat treatment to which it has been submitted. Low carbon steels are soft like wrought iron and are called *mild steel* (0.1 to 0.5% of carbon). Low and medium carbon steels are malleable and can be welded and forged like wrought iron. Steel has a high tensile strength. The hardness and tensile strength increase, and the malleability decreases, with increasing carbon content.

The hardness of steel can be modified by proper heat treatment. On being heated to redness and then plunged into cold water it becomes extremely hard (hardening of steel). The hardened steel may be softened to any desired extent by tempering i.e., heating it to a *selected* temperature between 230° to 300° and then allowing it to cool slowly. *The tempered steel* possesses the hardness and toughness required in razor blades, chisels, saws and springs.

Modern machine civilisation depends largely upon the numerous applications of iron and steel. Steel, for example, is used in making machine tools, implements of war and agriculture, rail lines, locomotives, cutlery, and magnets, etc.

Alloy steels.—Steels containing other metals alloyed with iron are known as alloy steels. The metals extensively used in alloy steels are Cr, Mn, Ni, V, W, Mo and Si. The alloying metals, usually added as ferro alloys, e.g., ferrochrome and ferromanganese, to the molten iron during recarburisation, imparts special properties on steel. The alloy steels are generally made in electric furnaces. Few alloy steels are :

Name	Alloying metal	Properties	Uses
Nickel steel	3.25% Ni ; 0.2—0.5%C	High elasticity and ductility.	Structural purposes.
Invar	35 per cent nickel	Low coefficient of expansion	Pendulum rod ; metre scale.
Platinite	46 per cent nickel	Same coefficient of expansion as glass	Glass to metal seals ; electric lamp bulbs.
Manganese-steel	12—13% Mn ; 0.9—2%C	Very hard ; resistant to wear	Jaws of rock crushers.
Chrome steel	0.5—2 per cent Cr	Very hard ; high tensile strength	Ball barings ; dies ; files.
Chrome-nickel steel	4% Ni ; 2% Cr ; 0.33%C	Retains temper & tensile strength	Armour plates ; motor cars.
Stainless steel	10—15% Cr ; 0.3%C	Resists corrosion ; rustless iron	Stainless cutlery ; valves ; turbine parts.
Chrome-vanadium steel	0.7—1.4% Cr ; 0.14—0.25% vanadium	High tensile strength ; resistance to stresses.	Automobile axles and springs.

Name	Alloying metal	Properties	Uses
High speed tool steel	18% tungsten; 5% Cr; 0.3% V; 0.7% C.	Retains temper & hardness at red-heat	High speed lathe tools.
Duriron, tant iron, ironac	About 16% Si	Resistant to acid corrosion	Acid-resisting vessels.
Allegheny	17-20% Cr; 7-10% Ni; 0.5% C; 0.5% Mn	High resistance to corrosion.	

Comparison of different varieties of iron.—The properties of iron depend largely upon the content of carbon. The properties of cast iron, steel and wrought iron are as follows:

Properties	*Cast iron*	*Steel*	*Wrought iron*
(i) *Amount of carbon*	2.2—4.5%	0.15 to 1.5%	0.12 to 0.25%
(ii) *Melting point*	1200°C	1300°—1400°C	1500°C
(iii) *Hardness*	Hard	Hard and soft	Soft
(iv) *Brittleness/malleability*	Brittle	Malleable/brittle	Malleable
(v) *Tempering*	Cannot be tempered	Can be tempered	Cannot be tempered.
(vi) *Welding*	Cannot be welded	Can be welded	Can be welded
(vii) *Magnetisation*	Cannot be permanently magnetised	Can be permanently magnetised	Cannot be permanently magnetised.

The Rusting of iron.—On exposure to ordinary moist air commercial iron becomes covered with a reddish-brown deposit of hydrated ferric oxide, mainly $2Fe_2O_3 . 3H_2O$, known as *rust*. *An impurity in the iron is necessary to cause rusting—pure iron does not rust.* It has been shown that the initial step in rusting is an electrolytic process—different parts of a specimen of iron act as poles of voltaic cells, the impurities setting up centres of rusting. At the anode iron passes into solution as ferrous ions, Fe^{++}, while at the cathode hydrogen ions (from the water : $H_2O \rightleftharpoons H^+ + OH^-$) are discharged.

At anode $Fe - 2e = Fe^{++}$
Iron dissolves

At cathode $2H^+ + 2e = H_2$
Hydrogen liberated.

For rusting to occur, the presence of liquid water and oxygen are essential; the water supplies the hydrogen ions, while the oxygen acts as a depolariser in oxidising the nascent hydrogen at the cathode to water.

The ferrous ions, Fe^{++}, which pass into solution as the initial step in rusting and the hydroxyl ions, OH^- (from water), combine to form ferrous hydroxide, which is then oxidised by the air and deposited as hydrated ferric oxide.

$$Fe + 2H^+ = Fe^{++} + H_2 ; \quad Fe^{++} + 2OH^- = Fe(OH)_2$$
$$2Fe(OH)_2 + O = Fe_2O_3,H_2O + H_2O$$

Rusting is greatly accelerated by carbon dioxide (since carbonic acid furnishes the H^+ ions) and metallic salts such as dissolved chlorides in the water, but it is retarded by alkalis. Hence the factors which influence rusting in moist air are : (i) the purity of the iron and the nature of its surface, (ii) the presence of dissolved substances in the water. Metals such as chromium and nickel which form solid solution with steel render it rustless.

Iron is usually protected from rusting by metallic coatings, e.g. tinning, galvanisation, nickel-plating, chromium-plating, etc. and by coatings of paints, varnishes, lacquers, enamels, coal tar, asphalt etc.

Properties of iron.—(i) Pure iron is a soft white metal which is highly tenacious, malleable and ductile. It is *magnetic.*

Pure iron may be obtained by electrolysis of an aqueous solution of ferrous chloride at 110° or by reducing ferric oxide in hydrogen at 1000°—*reduced iron* is pyrophoric.

(ii) Stable in dry air, it *rusts* in moist air. It burns brilliantly in oxygen when heated to redness, throwing off sparks of Fe_3O_4.

(iii) It is oxidised at a red heat by air or steam to ferroso-ferric oxide, Fe_3O_4 : $3Fe+4H_2O \leftrightharpoons Fe_3O_4+4H_2$.

(iv) It dissolves readily in dilute hydrochloric or sulphuric acid to give hydrogen and a *pale green ferrous salt :*

$$H_2SO_4+Fe = FeSO_4+H_2.$$

Iron also dissolves in dilute or fairly strong nitric acid (p. 138).

Passive iron.—Iron is rendered *passive* by immersion in concentrated nitric acid. The passive iron is insoluble in dilute acids and does not precipitate copper from a solution of copper sulphate. The passivity is due to the formation of a thin continuous film of Fe_2O_3 on the surface of iron ; passivity is removed by scratching the metal or by touching it with a piece of active iron under dilute sulphuric acid, or by heating it in hydrogen.

Iron also becomes passive in solutions of oxidising acids, e.g., chromic, chloric and iodic acids, and by anodic oxidation.

(v) It precipitates copper from a solution of copper sulphate :

$$CuSO_4+Fe = Cu+FeSO_4.$$

(vi) It combines directly, when heated, with carbon, sulphur, chlorine, yielding the *carbide*, Fe_3C, the ferrous sulphide, FeS, and the ferric chloride, $FeCl_3$, respectively. *Iron is not attacked by alkalis.*

Compounds of Iron.—Iron forms two series of compounds, e.g., *ferrous compounds* in which the metal is *divalent*, and *ferric compounds* in which the metal is *trivalent.* Ferrous salts gradually pass into the ferric state on exposure to air.

Ferrous salts are nearly colourless in solution, but usually possesses a *green* tinge. Ferric ions are almost colourless, but undissociated ferric chloride is yellow in colour.

Ferrous salts are readily oxidised to the ferric state : (i) by atmospheric oxygen, especially in presence of an acid or hydrogen peroxide.

$$4FeSO_4 + 2H_2SO_4 + O_2 = 2Fe_2(SO_4)_3 + 2H_2O$$

(ii) by chlorine or bromine, $2FeCl_2 + Cl_2 = 2FeCl_3$.

(iii) by boiling with aqua regia or nitric acid,

$$6FeSO_4 + 3H_2SO_4 + 2HNO_3 = 3Fe_2(SO_4)_3 + 2NO + 4H_2O.$$

Ferric salts are reduced to the ferrous state :

(i) by nascent hydrogen in acid solution, e.g., zinc and hydrochloric acid, acid, $FeCl_3 + H = FeCl_2 + HCl$.

(ii) by hydrogen sulphide or sulphur dioxide,

$$2FeCl_3 + H_2S = 2FeCl_2 + 2HCl + S.$$

$$2FeCl_3 + SO_2 + 2H_2O = 2FeCl_2 + H_2SO_4 + 2HCl.$$

(iii) by stannous chloride, $2FeCl_3 + SnCl_2 = 2FeCl_2 + SnCl_4$.

Detection of iron.—Dry tests : (i) An iron compound, mixed with sodium carbonate and heated on charcoal in the reducing flame, yields a black mass of iron which is attracted by a magnet.

(ii) When an iron compound is heated in a borax bead, the bead becomes *yellow* in the oxidising flame and *bottle green in the reducing flame.*

Wet tests.—Distinctive reaction of ferrous and ferric iron ; used ferrous sulphate and ferric chloride solution.

Reagents : solutions of :	*Ferrous salt*	*Ferric salt*
1. NH_4OH or NaOH	Green precipitate of ferrous hydroxide	Reddish-brown precipitate of $Fe(OH)_3$.
2. Potassium ferricyanide, $K_3Fe(CN)_6$	Deep blue precipitate (Turnbull's blue)	No precipitate but a brown solution.
3. Potassium ferro-cyanide, $K_4Fe(CN)_6$	White precipitate rapidly turning blue	Deep blue precipitate (Prussian blue)*
4. Ammonium thio-cyanate, NH_4CNS	No colouration	Blood-red-colouration.**

* The Prussian blue is ferric ferrocyanide, $Fe_4[Fe(CN)_6]_3$

$$4FeCl_3 + 3K_4[Fe(CN)_6] = Fe_4[Fe(CN)_6]_3 + 12KCl.$$

** The deep red colouration is due to the ferrithiocyanate ion, $[Fe(CNS)_6]'''$.

$$2FeCl_3 + 6NH_4CNS \rightleftharpoons Fe[Fe(CNS)_6] + 6NH_4Cl.$$

Exercises

1. Write notes on (i) flux, gangue, and slag, (ii) self-reduction process, (iii) calcination and roasting.

2. Give an outline of the method of extraction of sodium from *either* sodium chloride, *or* caustic soda. Mention the uses of the metal. What are its reactions with : hydrogen, ammonia, aluminium chloride, water, and oxygen.

3. How is caustic soda made electrolytically ? Mention its chief properties and uses. Describe the changes that take place when (i) caustic soda and (ii) ammonia are separately added to solutions of copper sulphate, ferric chloride, alum, and zinc sulphate. How would you show that caustic soda contains hydrogen ? *P. U.* 1961.

4. Describe the changes that occur when : (i) sodium nitrate solution is boiled with zinc dust and caustic soda, (ii) brine is electrolysed, (iii) carbon dioxide is bubbled into caustic soda solution, (iv) carbon dioxide is passed into ammoniacal brine. (v) white phosphorus is boiled with caustic soda solution, (vi) chlorine is led into caustic soda solution, (vii) ammonium chloride is treated with caustic soda.

5. How is sodium carbonate prepared by the Ammonia-Soda process ? What are the advantages of the process ? How is sodium carbonate converted into : (i) sodium bicarbonate, (ii) sodium hydroxide ? What is the difference between sodium carbonate and sodium bicarbonate ? Why do their solutions react alkaline ?

6. Outline the preparation of : quicklime, calcium carbide, and plaster of Paris, and describe the action of water on them. Also mention their uses.

7. How is bleaching powder prepared ? Mention its chief properties and uses. What happens when a sample of bleaching powder is left exposed to air ? What is meant by available chlorine of bleaching powder ?

8. Name the chief ores of zinc. How is the metal extracted and purified. Describe the action of nitric and caustic soda on zinc. State the uses of the metal. What happens when zinc is added to copper sulphate solution. *P. U.* 1961.

9. Explain what happens when : (i) zinc is added to nitric acid (ii) caustic soda is added to zinc sulphate solution, (iii) zinc is added to ferric sulphate solution containing sulphuric acid, (iv) quicklime is heated in chlorine, (v) water is sprayed on quick lime; (vi) slaked lime is treated with chlorine, (vii) lime is heated with sand, (viii) a suspension of bleaching powder is treated separately with

(a) dilute sulphuric acid, (b) carbon dioxide, (c) sodium carbonate.

10. What is the chief source of aluminium ? How is the metal extracted from it ? Mention the important properties and uses of the metal. Describe the reactions of aluminium with : (i) chlorine, (ii) caustic soda, (iii) ferric oxide, (iv) water, (v) air.

11. Outline the preparation of : (i) potash alum from bauxite, (ii) blue vitriol from copper scrap. Mention their chief properties and uses.

12. Explain what happens when : (i) a mixture of alumina and coke is heated in chlorine, (ii) sodium aluminate is shaken with ammonium chloride, (iii) caustic soda is added to a solution of potash alum, (iv) copper sulphate solution is treated with : (a) iron powder, (b) ammonia, (c) potassium iodide, (d) caustic soda.

13. Name, with formulae, the chief ores of iron. Describe the process of making pig iron, stating the main reactions that occur. Explain the changes that occur when a piece of iron is dipped in : (a) strong nitric acid, (b) copper sulphate solution, (c) ferric chloride solution containing hydrochloric acid. How is iron detected in solution ? *Calcutta* '57

14. Given metallic iron, how would you prepare from it : ferrous sulphate, ferric chloride, magnetic oxide of iron ? Make a note on rusting and passivity of iron.

15. What is the difference in composition between cast iron, steel and wrought iron. Describe their chief properties and uses. How is steel prepared by Bessemer process ?

XXIII

Chemical calculations

On density and specific gravity.—The *density* (*absolute density*) of a substance is its mass per unit volume, $d = m/v$,

where m is the mass, v the volume and d the density of a body.

The unit of volume in *C.G.S.* system is 1 c.c. ; hence the mass in grams, of 1 c.c. of a substance is its density ; e.g., 'the density of diamond is 3.52' means that the mass of 1 cubic centimetre of diamond is 3.52 grams.

The *normal density* of a gas is the mass in grams of one litre of the gas measured at N.T.P.

The normal density of hydrogen is 0.0899 *grm.*

The *relative* desity of a substance is the ratio of its density to the density of a standard substance *under identical conditions* of temperature and pressure.

In the case of *gases and vapours* the standard substance is generally *hydrogen* and occasionally *air or oxygen.* The relative density is often called the *vapour density* (p. 69). The vapour density may be converted from one standard to another in the following way :

$$\text{Vapour density } (H = 1) = \frac{\text{density of the gas}}{\text{density of hydrogen}}$$

$$= \frac{\text{density of the gas}}{\text{density of oxygen}} \times \frac{\text{density of oxygen}}{\text{density of hydrogen}}$$

$$\therefore \text{ density of a gas } (H = 1) = \text{density of the gas } (O = 1) \times \text{density of oxygen } (H = 1).$$

Also, density of a gas (H = 1) = density of the gas (air = 1) × density of air (H = 1).

As already stated (p. 70),

(a) the density of a gas (H = 1) = $\frac{\text{wt. of 1 litre of gas at N.T.P.}}{0.09 \text{ gm}}$

∴ wt. of 1 litre of a gas at N.T.P. = its density (H=1) × 0.09 gm.

∴ wt. of 1 litre of air at N.T.P. = 14.4 × 0.09 gm = 1.296 gm, since the density of air (H = 1) is 14.4

(b) *Gram molar volume of a gas is* 22.4 *litres at N.T.P.* i.e., *gram molecular weight of a gas occupies* 22.4 *litres at N.T.P.*

In the case of *liquids and solids*, the standard substance is *water* at 4°C ; the relative density is then called the *specific gravity*.

In *C.G.S.* system, the absolute density of water at 4°C is unity. Hence the *specific gravity of a substance is numerically equal to its density* ; e.g., the absolute density of mercury is 13.6, the figure 13.6 also indicates its specific gravity.

Percentage.—By percent is meant parts in 100 parts. In the case of *solids*, percentage always refers to *weight* ; e.g., "a mineral of copper contains 2.5 per cent copper" means that 100 parts by weight of the mineral contain 2.5 parts by weight of copper.

In the case of *solutions*, percentage refers either (i) to the weight of a substance *per* 100 *parts by weight of the solution*, or (ii) to the weight in grams of a substance *per* 100 *c.c. of the solution* ; e.g., "a 20 per cent sulphuric acid" may either mean (i) 20 gms. of sulphuric acid per 100 gms. of the solution, or (ii) 20 gms. of sulphuric acid per 100 c.c. of the solution. The context alone will decide which meaning is applicable.

In the case of *gases*, percentage generally refers to *volume*, unless otherwise stated.

Exercises

(1) Calculate the weight of 10 litres of carbon dioxide measured at 0°C and 722 mm. pressure.

The molecular weight of CO_2 is 44, and its density (H = 1) is 22.

Let the volume of CO_2 at N.T.P. = v litres.

∴ $v \times 760/273 = 10 \times 722/273$, whence v = 9.5 litres.

The molar volume of a gas is 22.4 litres at N.T.P.

∴ 22.4 litres of carbon dioxide at N.T.P. weigh 44 gms.

∴ 9.5 litres of CO_2 at N.T.P. weigh $44 \times 9.5/22.4 = 18.60$ gms.

2. Calculate the volume occupied by 6.4 gms. of sulphur dioxide measured : (i) at N.T.P., (ii) at 273°C and 950 mm. pressure.

The molecular weight of SO_2 is 64, and hence the density (H = 1) is 32.

64 gms. of SO_2 occupy 22.4 litres at N.T.P.

∴ 6.4 gms. of SO_2 occupy 2.24 litres at N.T.P.

Let the volume at 273°C and 950 mm. be v litres

∴ $v \times 950/546 = 2.24 \times 760/273$, whence v = 1.792 litres.

3. A sample of gas weighing 0.1100 gm. occupies a volume of 24 c.c. at 27°C and 740 mm. pressure. Calculate the molecular weight of the gas.

Let the volume of the gas at N.T.P. = v c.c.

∴ $v \times 760/273 = 24 \times 740/300$, whence v = 21.26 c.c.

Molar volume of a gas = 22400 c.c. at N.T.P.

21.26 c.c. of the gas weigh 0.11 gm.

∴ 22400 c.c. of the gas weigh $0.11 \times 22400/21.26$ or 115.9 gm.

∴ gram molecular weight of the gas = 115.9 gm.

4. Determine the density of air (H = 1), supposing it to be a mixture of 4 volumes of nitrogen and one volume of oxygen. Given the densities (H = 1) of oxygen and nitrogen are, respectively, 16 and 14.

Weight of 100 volumes of air = weight of 80 volumes of nitrogen+weight of 20 volumes of oxygen.

∴ $100 \times$ density of air $= 80 \times 14 + 20 \times 16$, or density of air = 14.4.

5. Find the weight of 6.229 litres of oxygen (density 16) measured at 27°C and 750 mm. pressure. Normal density of hydrogen is 0.089 gm. 7.968 gm.

6. 2.257 litres of a gas at 27°C and 740 mm. weigh 2.857 gm. Find its density. Normal density of hydrogen is 0.089 gm.

Normal density = 1.428 gm. Density (H = 1) = 16.

7. The density of carbon dioxide relative to air is 1.528. Find its density relative to hydrogen. 22.

8. Calculate the volume occupied by 1.7 gms. of ammonia : (i) at N.T.P., (ii) at 27°C and 740 mm. pressure. (i) 2.24*l*. (ii) 2.527*l*.

9. A sample of gas weighing 0.8 gm. occupies 1247 c.c. at 27°C and 750 mm. Calculate the molecular weight of the gas. 16

10. A litre of sea water (sp. gr. 1.03) is evaporated to dryness and found to give as residue 36.4 gms. of salt ; find the percentage of solid matter per 100 gms. of sea water. 3.534%.

11. A sample of sulphuric acid contains 31.6 gm. of pure acid per 100 gm. of the acid solution and its specific gravity is 1.26. Calculate the weight of real acid in every 100 c.c. of the solution. 39.8 gm.

12. Calculate weight of pure HNO_3 in 10 c.c. of commercial nitric acid (sp. gr. 1.4) containing 65% HNO_3 by weight. 9.1 gm.

On percentage composition.—(i) **Composition from formula.**—The percentage composition of a compound states the weight of each constituent in 100 parts by weight of the substance. In order to determine it :

(a) find the molecular weight (i.e., the sum of the atomic weights of all the constituent atoms) of a compound, represented by its formula, and then :

(b) divide the total weight of each constituent by the molecular weight and multiply by 100.

(i) Calculate the percentage composition of anhydrous sodium sodium sulphate. Its molecular formula is Na_2SO_4 :

wt. of 2 atoms of sodium $= 2 \times 23 = 46$

wt. of 1 atom of sulphur $= 1 \times 32 = 32$

wt. of 4 atoms of oxygen $= 4 \times 16 = 64$

∴ molecular weight of $Na_2SO_4 = 46 + 32 + 64 = 142$.

Now, 142 part by wt. of Na_2SO_4 contain 46 parts of wt. of sodium.

∴ 100 ,, ,, ,, $46 \times 100/142$ or 32.4 ,, ,, ,,

∴ % of sodium = 32.40

Similarly, % of sulphur $= 32 \times 100/142 = 22.53$; % of oxygen = 45.07

(ii) Calculate the percentage of iron, NH_4 and SO_4 groups and water in ferric ammonium sulphate of the formula, $(NH_4)_2SO_4, Fe_2(SO_4)_3, 24H_2O$.

Molecular weight from formula :

wt. of 2 atoms of Fe $= 2 \times 56 = 112.0$
wt. of 3 SO_4—groups $= 3 \times 96 = 228.0$
wt. of 2 NH_4— ,, $= 2 \times 18 = 36.0$
wt. of 1 SO_4— ,, $= 1 \times 96 = 96.0$
wt. of 24 H_2O ,, $= 24 \times 18 = 432.0$
Total $= 964.0$

In 964 gm. of the compound there are 112 gms. of iron.

$\therefore$ in 100 ,, ,, ,, $112 \times 100/964$ or 11.62 gms. of iron...

$\therefore$ % of Fe $= 11.62$

Similarly, % of $NH_4 = (36 \times 100)/964 = 3.73$
% of $SO_4 = (4 \times 96 \times 100)/964 = 39.83$
% of water $= (432 \times 100)/964 = 44.82$

(ii) **Formula from percentage composition.**—The formula of a compound is deduced by finding the number of atoms of each constituent element from its percentage composition.

Suppose the formula of a compound containing the elements A (at wt. a) and B (at. wt. b) is A_xB_y, where x and y are the number of atoms of A and B respectively.

$\therefore$ % of A $= ax.\ 100/(ax+by)$, and % of B $= by.\ 100/(ax+by)$.

$$\frac{\%\text{ of A}}{\%\text{ of B}} = \frac{ax}{by} \quad \text{or} \quad \frac{\%\text{ of A}}{a} : \frac{\%\text{ of B}}{b} = x : y$$

i.e., $\dfrac{\%\text{ of A}}{\text{at. wt. of A}} : \dfrac{\%\text{ of B}}{\text{at wt. of B}} =$ number of atom of A : number of atom of B.

i.e., the quotient of the percentage of each element divided by its atomic weight is a number which is proportional to the number of atoms in the compound.

Hence to deduce the formula from percentage composition :

(i) divide the percentage of each element by its atomic weight to obtain the ratio of number of atoms of each element ;

(ii) divide each number as obtained in (i), by the smallest of them and then multiply the quotients, if necessary, by a small number, in order to express the ratio in the simple whole numbers, since fractional atoms are inadmissible.

The formula of a compound directly deduced from its percentage composition is called the **simplest** or **empirical formula.** It simply shows the relative number of atoms of each element present in the compound.

The **molecular formula,** on the other hand, gives the *exact* number of atoms of each element in a molecule. Hence the molecular formula is either equal to or some multiple of the empirical formula. Let the empirical formula of a compound be A_pB_q, then :

$$(A_pB_q)_n = \text{molecular formula.}$$

or $(ap+bq)n$ = molecular weight $= 2 \times$ vapour density $(H = 1)$.

$\therefore$ $n = \dfrac{2 \times \text{vapour density}}{ap+bq}$, where a, b are the atomic weights and p and q are the atoms of A and B respectively in the empirical formula A_pB_q, and n is a simple integer.

Exercises

1. A compound of C, H and O contains C = 40% H = 6.67%. Its molecular weight is 180. Find its formula. *Calcutta* '38.

C = 40%, H = 6.67% $\therefore$ O = 100−(40+6.67) = 53.33%.

Dividing the percentage of each element by its atomic weight

C = 40/12 = 3.33, H = 6.67/1 = 6.67, O = 53.33/16 = 3.33.

These numbers are proportional to the number of atoms of the elements present in one molecule of the compound.

Dividing the numbers by the lowest number to transform them into whole numbers, since fractional atoms are inadmissible.

C=3.33/3.33 = 1, H = 6.67/3.33 = 2, O = 3.33/3.33 = 1

$\therefore$ the simplest formula is CH_2O and the molecular formula is $(CH_2O)n$. Now, the molecular weight is 180.

$\therefore$ $(CH_2O)n = 180$, or $(12+2+16)n = 180$, whence n=6.

Hence the molecular formula is $(CH_2O)_6$ or $C_6H_{12}O_6$.

2. A compound containing Na, S, O and H gave on analysis the following result: Na= 14.31% S = 9.97% H= 6.25% O = 69.47%. Calculate the formula on the assumption that all the hydrogen in the compound is present in combination with oxygen as water. *Calcutta* '18.

Dividing by atomic weights :

Na = 14.31/23 = 0.62, S = 9.97/32 = 0.31,
H = 6.25/1 = 6.25, O = 69.47/16 = 4.24.

Dividing the quotients by the lowest number :

Na = 0.62/0.31 = 2, S = 0.31/0.31 = 1,
H = 6.25/0.31 = 20, O = 4.34/0.31 = 14.

Hence the formula is $Na_2SH_{20}O_{14}$. But all the hydrogen is present in combination with oxygen as water, 20 atoms of hydrogen combine with 10 atoms of oxygen to form $10H_2O$. Hence the formula is Na_2SO_4, $10H_3O$.

3. Two oxides of a metal contain 27.6 and 30% oxygen respectively. If the formula of the first oxide be M_3O_4, find that of the second. *Cal.* '40.

Let a be the atomic weight of the metal M. The first oxide contains 27.6% oxygen, and (100−27.6) or 72.4% of the metal.

$$\frac{\%\text{ of M}}{\text{at wt. of M}} \Big/ \frac{\%\text{ of }O_2}{\text{at. wt. of }O_2} = \frac{\text{No. of atoms of M}}{\text{No. of atoms of }O_2}$$

or $72.4/a : 27.6/16 = 3 : 4$; whence $a = 55.97$.

The second oxide contains 30% O_2 and 70% M.

$$\frac{\text{No. of atoms of M}}{\text{No. of atoms of }O_2} = \frac{70}{55.97} \Big/ \frac{30}{16} = \frac{1.25}{1.87} = \frac{1}{1.5} = \frac{2}{3}$$

since atoms cannot be divided ; $\therefore$ the formula of the oxide is M_2O_3.

Assume the following atomic weights : K = 39.1, Cl = 35.5, Mg = 24, H = 1, Al = 27, Na = 23, Pb = 207, Cu = 63.5, P = 31.

4. Determine the percentage composition of: (*a*) potassium chlorate, (*b*) Epsom salt ($MgSO_4, 7H_2O$), (*c*) cryolite ($AlF_3, 3NaF$).

(*a*) K 31.89 ; Cl 28.95 ; O 39.16 ; (*b*) Mg 9.76 ; S 13.01 ; O 26.01 ; H_2O 51.22 ; (*c*) Na 32.86 ; Al 12.86 ; F 54.28.

5. Calculate the percentage of—(*a*) lead in white lead ($2PbCO_3, Pb(OH)_2$), (*b*) chlorine in carnallite ($KCl, MgCl_2, 6H_2O$), (*c*) nitric anhydride (N_2O_5) in potassium nitrate, (*d*) water of crystallisation in blue vitriol, (*e*) carbon dioxide in calcium carbonate.

(*a*) 80.13 ; (*b*) 38.36 ; (*c*) 53.40 ; (*d*) 36.07 ; (*e*) 44.

6. Water contains 11.11% hydrogen and 88.88% oxygen. Calculate its formula. H_2O

7. A compound of C, H and O contains 42.105% carbon, 6.432% hydrogen and the rest oxygen. Its molecular weight is 342. Calculate the formula. $C_{12}H_{22}O_{11}$

8. A compound contains 82.74% carbon and 17.26% hydrogen. Its vapour density is 29. Find the formula. C_4H_{10}

9. A crystalline salt contains 18.55% sodium, 25.81% sulphur, 19.35% oxygen (which is not present as water) and 36.29% water of crystallisation. What is its formula ? $Na_2S_2O_3.5H_2O$.

10. 12.325 gm. of Epsom salt lose 6.306 gms. of water on dehydration and leave behind $MgSO_4$. Calculate the formula of Epsom salt.

Banaras '27. $MgSO_4, 7H_2O$.

11. A compound was found on analysis to have the following composition : $K = 17.8$; $Ni = 13.5$, $SO_4 = 44$, $H_2O = 24.7\%$. What is its formula?

$Ni = 58.7$. *Bombay* '18. $K_2SO_4, NiSO_4, 6H_2O$.

12. Calculate the molecular formula from the results of analysis given : S—23.7%, Cl—52.6% and the rest being oxygen. Vapour density = 67.5. SO_2Cl_2.

13. A substance has the following percentage composition : N—35, H—5, O—60. On being heated it yields a gas containing N 63.63% and O 36.37%. Calculate the formula of each substance. Name the original substance and construct the equation representing the chemical change.

Andhra University. NH_4NO_3, N_2O ; $NH_4NO_3 = N_2O + 2H_2O$.

14. Express the percentage composition of crystallised sodium carbonate, $Na_2CO_3, 10H_2O$, in terms of : (a) anhydrous sodium carbonate and water of crystallisation, and (b) Na_2O. Calculate the percentage of Na_2O in anhydrous sodium carbonate. (a) H_2O 62.94 ; Na_2CO_3 37.06 ; (b) 21.68 ; 58.49.

15. An element *X*, forms a hydride containing 25 per cent of hydrogen ; *X* also forms two oxides *A* and *B*, containing 57.1 and 72.7 per cent of oxygen respectively. The atomic weight of the element is 12. Find the formulae of the hydride and the two oxides. XH_4 ; XO, XO_2.

On chemical equations.—The following informations will be found useful in the chemical calculations :

(i) *All reactions represented by chemical equations are assumed to take place at N.T.P., i.e., at* 0°C *and* 760 *mm. pressure :*

(ii) *The weight of* 1 *litre of hydrogen at N.T.P.* = 0.0899 *gm.*

Density of air (relative to hydrogen) is 14.4.

Weight of 1 litre of air at N.T.P. = $14.4 \times 0.0899 = 1.295$ gms.

(iii) *Molecular weight of a gas* = 2 × its vapour density (H = 1).

Vapour density of a gas (H = 1) = its vapour density (O = 1). × vapour density of oxygen (H = 1).

(iv) *Mass = volume × density.*

(v) *Atomic weight = equivalent weight × valency.*

(vi) $PV/T = P'V'/T'$ where P, V, T and P′, V′, T′ are the pressure, volume and temperature of a gas under two sets of conditions.

For *moist gases*, the barometric pressure (P) = pressure of the gas (p) + aqueous tension (f) at the temperature at which the gas is collected : $\therefore\ p = P - f$.

(vii) Atoms and molecules stand for gram-atoms and gram-molecules, i.e., atomic weight and molecular weight expressed in grams.

(viii) *In the synthesis of water from its elements, two-thirds the contraction = the volume of hydrogen, and one-third the contraction = the volume of oxygen.*

(ix) One gram molecule of a gas occupies 22.4 litres at N.T.P.

Exercises

(*a*) **Gravimetric analysis.**—*Calculations involving chemical equations, but not introducing gas volumes.*

(1) How much carbon is required to reduce 165 gms. of CO_2 to CO ?

$$\underset{44}{CO_2} + \underset{12}{C} = 2CO$$

44 gm. CO_2 are reduced by 12 gm. carbon.

∴ 165 gm. CO_2 are reduced by 45 gm. carbon.

(2) What weight of chalk must be decomposed by HCl to yield sufficient CO_2 to convert 50 gm. of NaOH to sodium carbonate.

$$\underset{2\times40}{2NaOH} + \underset{44}{CO_2} = Na_2CO_3 + H_2O.$$

80 gm. of NaOH react with 44 gm. of CO_2

∴ 50 gm. of NaOH react with 55/2 gm. of CO_2

$$\underset{100}{CaCO_3} + 2HCl = CaCl_2 + H_2O + \underset{44}{CO_2}$$

44 gm. of CO_2 are obtained from 100 gm. of $CaCO_3$

55/2 gm. of CO_2 are obtained from 62.5 gm. of $CaCO_3$

∴ weight of chalk required = 62.5 gm.

3. 8 gms. of pure manganese dioxide are heated with an excess of HCl and the gas evolved is passed into a solution of KI. Calculate the weight of iodine liberatred. Molecular weight of $MnO_2 = 55+2\times16 = 87$. *Nagpur* '33.

$$\underset{87}{MnO_2}+4HCl = MnCl_2+2H_2O+\underset{71}{Cl_2}\ ; \quad 2KI+\underset{71}{Cl_2} = 2KCl+\underset{2\times127}{I_2}$$

87 gms. of MnO_2 produce 71 gms. of chlorine

∴ 8 gms. ,, ,, 71×8/87 or 6.528 gm. of chlorine.

35.5 gm. chlorine liberate 127 gm. of iodine.

∴ 6.528 gm. ,, ,, 127×6.528/35.5 or 23.35 gm. of iodine.

∴ the weight of iodine liberated = 23.35 gms.

4. How much potassium chlorate must be strongly heated to yield as much oxygen as would be obtained from 200 gms. of mercuric oxide ? *Calcutta*, '46.

Molecular weight of $KClO_3$ = 122.5, and that of HgO = 216.

$$\underset{432}{2HgO} = 2Hg + \underset{32}{O_2}\,; \qquad \underset{245}{2KClO_3} = 2KCl + \underset{96}{3O_2}$$

432 gms. of HgO produce 32 gms. of oxygen.

∴ 200 gms. ,, ,, $32 \times 200/432$ or 14.8 gm of oxygen.

96 gms. of oxygen are obtained from 245 gms. of $KClO_3$

∴ 14.8 gms. ,, ,, ,, ,, $245 \times 14.8/96$ or 37.78 gm of $KClO_3$

∴ the amount of $KClO_3$ required = 37.78 gms.

5. 1.84 gms. of a mixture of $CaCO_3$ and $MgCO_3$ is strongly heated till no further loss of weight takes place. The residue weighs 0.96 gm. Calculate percentage composition of the mixture. *U. P. Board* '43.

Let the weight of $CaCO_3 = x$ gms., then the wt. of $MgCO_3 = (1.84 - x)$ gms.

$$\underset{100}{CaCO_3} = \underset{56}{CaO} + CO_2$$

i.e., 100 gms. of $CaCO_3$ leave a residue of 56 gms. of CaO.

∴ x gms. ,, ,, ,, $56x/100$ gm. of CaO.

$$\underset{84}{MgCO_3} = \underset{40}{MgO} + CO_2$$

i.e., 84 gms. of $MgCO_3$ leave a residue of 40 gms. of MgO.

∴ $(1.84 - x)$ gms. leave a residue of $40(1.84 - x)/84$ gm. of MgO.

∴ $\frac{56x}{100} + \frac{40(1.84 - x)}{84} = 0.96$, whence $x = 1$.

∴ % of $CaCO_3 = 1 \times 100/1.84 = 54.35$;

% of $MgCO_3 = 0.84 \times 100/1.84 = 45.65$.

(b) Calculations on equations involving gas volumes.—

6. You are given a balloon with a capacity of 1000 litres and you are to fill it with hydrogen at 30°C and 550 m.m. pressure. How much iron would you require for the purpose ? *Banaras* '22.

Let 1000 litres of H_2 at 30°C and 750 m.m. occupy v litres at N.T.P.

∴ $\frac{1000 \times 750}{30 + 273} = \frac{v \times 760}{273}$ whence $v = 889.4$ litres.

(i) $\underset{3 \times 56}{3Fe} + 4H_2O = Fe_3O_4 + \underset{4 \times 22.4 \text{ litres at N.T.P.}}{4H_2}$

i.e., 4×22.4 litre of H_2 at N.T.P. require 3×56 gm of Fe

∴ 889.4 litre of H_2 at N.T.P. $(3 \times 56 \times 889.4)/422.4$ or 1667 gm of Fe.

(ii) $\underset{56}{Fe} + H_2SO_4 = FeSO_4 + \underset{22.4 \text{ litres at N.T.P.}}{H_2}$

i.e., 22.4 litres of H_2 at N.T.P. require 56 gm of Fe

∴ 889.4 litres of H_2 at N.T.P. require $(56 \times 889.4)/22.4$ or 2224 gm. of Fe.

∴ iron required is 1667 gm. or 2224 gm. according as Fe reacts with steam or acid.

7. Calculate the amount of $KClO_3$ which on complete decomposition will yield just sufficient oxygen for the complete combustion of 1520 c.c. of a gas mixture, consisting of 20 per cent methane and 80 per cent carbon monoxide at 27°C and 750 m.m. pressure. *Calcutta* '44.

Suppose the volume of the gas mixture is v c.c. at N.T.P.

∴ $\frac{v \times 760}{273} = \frac{1520 \times 750}{300}$ whence $v = 1365$ c.c.

Vol. of $CH_4 = 1365 \times 0.2 = 273$ c.c. ; vol. of $CO = 1365 \times 0.8 = 1092$ c.c.

(*i*) $CH_4 + 2O_2 = CO_2 + 2H_2O$
1 vol. 2 vols.

i.e., 1 c.c. of methane at N.T.P. ia burnt by 2 c.c. of O_2 at N.T.P.

∴ 273 ,, ,, ,, ,, are burnt by 546 c.c. of O_2 at N.T.P.

(*ii*) $2CO + O_2 = 2CO_2$
2 vols. 1 vol.

i.e., 2 c.c. of CO at N.T.P. are burnt by 1 c.c. of O_2 at N.T.P.

∴ 1092 c.c. of CO at N.T.P. are burnt by 546 c.c. of O_2 at N.T.P.

∴ total volume of oxygen required = 546 + 546 = 1092 c.c.

Now, $2KClO_3 = 2KCl + 3O_2$
245 gm. 3×22.4 litres at N.T.P.

i. e. 3×22400 c.c. of O_2 are obtained from 245 gm. or $KClO_3$.

∴ 1092 c.c. ,, ,, ,, ,, $\dfrac{245 \times 1092}{3 \times 22400}$ or 3.98 gm.

8. A sample of 25 gms. of pure chalk were uniformly mixed with pure silica ; 0.75 gms. of the mixture when treated with hydrochloric acid liberated 125 c.c. of CO_2, measured at 27°C and 756 m.m. pressure. Find the amount of silica that was mixed with the sample of chalk.

Suppose the volume of CO_2 at N.T.P. is v. c.c., then

$\dfrac{v \times 760}{273} = \dfrac{125 \times 756}{300}$ whence v = 113.2 c.c.

$CaCO_3 + 2HCl = CaCl_2 + H_2O + CO_2$
100 22400 c.c.

i.e., 22400 c.c. of CO_2 are liberated from 100 gms. of chalk.

∴ 113.2 c.c. ,, ,, ,, 113.2/22.4 or 0.5 gm. of chalk.

∴ 0.75 gm. of the mixture contained 0.5 gm. of chalk, and hence 0.75--0.5 = 0.25 gm. of silica.

Hence, 0.5 gm. of chalk was mixed with 0.25 gm. of silica

or 25 gm. ,, ,, ,, ,, 12.5 gm. ,,

∴ the amount of silica = 12.5 gms.

9. 0.0321 gm. of an impure sample of aluminium gave on treatment with dilute hydrochloric acid 39.3 c.c. of moist hydrogen measured at 13°C and 761 m.m. pressure. The impurity in the sample was alumina. Calculate the percentage of purity of the metal. Aqueous tension at 23°C=11 m.m. *Cal.* '46

Let the volume of hydrogen at N.T.P. be v c.c., then

$\dfrac{v \times 760}{273} = \dfrac{39.3 \times (761 - 11)}{(273 + 13)}$, whence v = 37 c.c.

$2Al + 6HCl = 2AlCl_3 + 3H_2$

2×27 gm. 3×22.4 litres at N.T.P.

∴ 37 c.c. of hydrogen correspond to $(2 \times 27 \times 37)/3 \times 22400$ gms. of aluminium, i.e., 0.02973 gm. of Al.

Hence, the impurity = (0.0321 − 0.02973) = 0.00237

∴ the % of impurity = $(0.00237 \times 100)/0.0321 = 7.38\%$.

10. How many c.c.'s of hydrogen and oxygen at 10°C and 770 mm. pressure can be obtained from 1 gram of water ? H 1273 c.c. ; O 636.5 c.c.

11. What weight of potassium chlorate is required to yield oxygen sufficient to burn the hydrogen evolved by the action of water upon 230 gms. of sodium ? 204.2 gm.

12. How much marble and hydrochloric acid containing 22 per cent HCl are required to give 10 litres of CO_2 at 15°C and 760 m.m. pressure ?
42.32 gm. marble ; 140.5 gm. HCl solution.

13. 2.5 litres of nitrous oxide are collected at 39°C and 741 mm. pressure. What weight of ammonium nitrate are decomposed in order to supply the gas ? 7.6 gm.

14. 5 gms. of manganese dioxide are heated with excess of HCl. The chlorine evolved is passed into potassium iodide solution. Calculate the weight of iodine liberated. *Bombay* '14. 14.60 gms.

15. Three grams of a mixture of anhydrous sodium carbonate and sodium bicarbonate lost 0.348 gm. on heating. Calculate the percentage of sodium carbonate in the mixture. 68.567.

16. Calculate the volume of hydrogen at 27°C and 750 mm. pressure that would be produced in each of the following cases by the decomposition of 5.4 gms. of water when (a) water is acted upon by sodium, (b) water reacts with calcium hydride, (c) steam is pased over red hot iron.
(a) 3.74 ; (b) 7.48 ; (c) 7.48 litres. *Calcutta* '41.

17. A balloon of 1000 litres capacity is to be filled with hydrogen at 27°C and 750 mm. pressure. Calculate the minimum quantity of iron required to liberate the necessary amount of hydrogen. *Calcutta* '25.
1684 gms. of Fe by steam-iron process.

18. Calculate the quantity of pure $CaCO_3$ from which one litre of CO_2 at 27°C and normal pressure may be prepared. What weight of pure carbon would yield the same quantity of CO_2 ? *Calcutta* '29. $CaCO_3$, 4 gm. ; Carbon 0.49 gm.

19. Find the weight of $KClO_3$ necessary to prepare 1 litre of oxygen at 27°C and 750 mm. pressure. 3.275 gms. of $KClO_3$.

20. What volume of carbon dioxide could be obtained by dissolving 3 gms. of pure marble in hydrochloric acid ? What volume would the gas occupy at 16°C and 750 mm. ? 672 c.c. ; 720.7 c.c.

21. 1.000 gm. of a mixture of the carbonates of calcium and magnesium gave 240 c.c. of CO_2 at N.T.P. Calculate the composition of the mixture.
62.5% $CaCO_3$; 37.5% $MgCO_3$.

22. 4.5 gms. of water are (a) decomposed by sodium ; (b) passed as steam over red hot iron ; (c) decomposed by an electric current. What volume of gas at N.T.P. is produced in each case ? *Calcutta* '27. 2.8 litres ; 5.6 litres ; 8.4 litres.

23. How much ammonia would you get from 1 gm. of NH_4Cl at 15°C and 740 mm. ? *Calcutta* '16. 453.5 c.c.

Eudiometry

Eudiometry refers to reactions taking place in the gas phase only and hence is concerned with the *analysis of gases* and *volumetric composition of gaseous compounds*. The equation :

$$2H_2 + O_2 = 2H_2O \text{ (steam)}$$

signifies that 2 gram molecules of hydrogen combine with 1 gram molecule of oxygen to form 2 gram molecules of steam, or 2×22.4 litres of hydrogen combine with 22.4 litres of oxygen to form 2×22.4 litres of steam—*the volumes being all measured at N.T.P.*

$\therefore$ the *relative* volumes of hydrogen, oxygen and steam in the above reaction is $H_2 : O_2$: steam is 2 : 1 : 2 *by volume*.

In eudiometry, for comparison of volumes of gases involved in a reaction, the knowledge of their relative volumes (and not of the actual volumes) is required, and *for convenience* 1 *gram-molecule of a gas is supposed to occupy one volume* (which, however, stands for 22.4

litres at N.T.P.). Hence the equation $2H_2+O_2=2H_2O$ (steam) shows that 2 volumes of hydrogen unite with one volume of oxygen to give 2 volumes of steam.

Illustrations.—(i) $2H_2 + O_2 = 2H_2O$ (steam) Contraction
2 vols. 1 vol. 2 vols. 1 volume

When the temperature of the eudiometer is below 100°C, steam condenses into water of negligible volume, and hence *the contraction becomes* 3 *volumes.*

2/3rds the contraction = the volume of hydrogen ;
1/3rd the contraction = the volume of oxygen.

(ii) $CH_4 + 2O_2 = CO_2 + 2H_2O$ (liquid) Contraction
1 vol. 2 vols. 1 vol. 0 vol. 2 volumes.

(iii) $2C_2H_2 + 5O_2 = 4CO_2 + 2H_2O$ (liquid)
2 vols. 5 vols. 4 vols. 0 vol. 3 volumes.

(iv) $C_2H_4 + 3O_2 = 2CO_2 + 2H_2O$ (liquid)
1 vol. 3 vols. 2 vols. 0 vol. 2 volumes.

(v) CO_2 + C (solid) = 2CO Expansion.
1 vol. 0 vol. 2 vols. 1 volume.

(vi) $N_2 + O_2 = 2NO$
1 vol. 1 vol. 2 vols. No change in volume.

The volume occupied by a *liquid* or a *solid* is negligibly small compared with that of a gas ; they are therefore, supposed to occupy *zero volume* in eudiometry.

In *gas analysis* the volumes of gases, may be found out by absorption with suitable absorbents.—(i) *caustic potash for CO_2 and other acid gases,* (ii) *alkaline pyrogallate for oxygen,* (iii) *ammoniacal cuprous chloride for CO and acetylene* and (iv) *fuming H_2SO_4 or bromine water for ethylene.* Volume of methane is found out by explosion with oxygen.

The formula of gaseous hydrocarbons.—The formula of a gaseous hydrocarbon is determined by exploding a known volume of it with excess oxygen—the immediate contraction on explosion and also the contraction that occurs when caustic potash is admitted (thus absorbing the carbon dioxide formed) are being noted.

Contraction on explosion = (volume of gases before explosion) —(volume of gases after explosion)

i.e., contraction = (vol. of hydrocarbon+vol. of oxygen *taken*)— (vol. of carbon dioxide formed+vol. of oxygen *left unused*).

or contraction=vol. of hydrocarbon+(vol. of oxygen *taken*—vol. of oxygen *left* unused)—vol. of carbon dioxide formed.

∴ **contraction on explosion = vol. of hydrocarbon + vol. of oxygen actually used up—vol. of carbon dioxide formed.**

Exercises

1. 20 c.c. of a gaseous hydrocarbon were exploded with excess of O_2. The contraction observed was 30 c.c. There is a further contraction of 40 c.c. on treatment with KOH. What is the molecular formula of the hydrocarbon ? *Calcutta* '48.

Contraction on explosion = vol. of the hydrocarbon+vol. of O_2 used up—vol. of CO_2 formed.

∴ 30 = 20+vol. of O_2 used up −40 ∴ vol. of O_2 used up = 50 c.c.

Now, CO_2 contains its own volume of O_2. $C+O_2 = CO_2$.

∴ 40 c.c. CO_2 formed contain 40 c.c. O_2, i.e., 40 c.c. of O_2 were used to oxidise the carbon in the hydrocarbon.

∴ the oxygen used in oxidising the hydrogen of the hydrocarbon $= (50-40)$ $= 10$ c.c.

∴ vol. of hydrogen = twice the volume of $O_2 = 2 \times 10 = 20$ c.c.

20 c.c. of the hydrocarbon contain this 20 c.c. of hydrogen.

Hence, 20 c.c. of the hydrocarbon contain 20 c.c. of H_2 and give 40 c.c. of CO_2.

∴ 1 c.c. of the hydrocarbon contains 1 c.c. of H_2 and gives 2 c.c. of CO_2.

or, 1 molecule of the hydrocarbon contains 1 molecule of hydrogen and give 2 molecules of CO_2.

Now, 1 molecule of hydrogen consists of 2 atoms of hydrogen and 1 molecule of CO_2 contains 1 atom of carbon. ∴ the formula is C_2H_2.

2. 25 c.c. of marsh gas at N.T.P. are mixed with 300 c.c. of air at 27°C and 750 mm. pressure and the mixture is exploded by electric sparks. Find out the volume of the residual gas at 17°C and 750 mm. pressure. Air contains 20% O_2 and 80% N_2 by volume. *Calcutta* '16.

Let 300 c.c. of air at 27°C and 750 mm. occupy v c.c. at N.T.P.

$$\therefore \quad \frac{v \times 760}{273} = \frac{300 \times 750}{300} \text{ whence } v = 269.4 \text{ c.c.,}$$

269.4 c.c. of air contains $\frac{20 \times 269.4}{100}$ or 53.88 c.c. of O_2 and $\frac{80 \times 269.4}{100}$ or 215.52 c.c. of nitrogen at N.T.P.

The reaction involved is

$$\begin{array}{ccccccc} CH_4 & + & 2O_2 & = & 2H_2O & + & CO_2 \\ 1 \text{ c.c.} & & 2 \text{ c.c.} & & & & 1 \text{ c.c.} \end{array}$$

∴ 25 c.c. CH_4 consumes 50 c.c. of O_2 and yield 25 c.c. of CO_2.

∴ the volume of the oxygen left unused $= (53.88-50) = 3.88$ c.c. Final volume of the gas mixture $= 215.52$ c.c. of $N_2 + 3.88$ c.c. of $O_2 + 25$ c.c. $CO_2 = 244.4$ c.c. at N.T.P.

Let the mixture occupy v c.c. at 17°C and 750 mm.

$$\therefore \quad \frac{v \times 750}{290} = \frac{244.4 \times 760}{273} \text{ whence } v = 265 \text{ c.c.}$$

3. One litre of a mixture of CO and CO_2 is found to give 1600 c.c. of CO on being passed through a tube containing red-hot charcoal, both measured under the same conditions. Calculate the composition of the mixture. *Calcutta* '14.

Let the vol. of CO_2 in the mixture be x c.c.,

∴ vol. of CO is $(1000-x)$ c.c.

The reduction of CO_2 takes place as follows :

$$\begin{array}{ccccc} CO_2 & + & C & = & 2CO \\ 1 \text{ c.c.} & & & & 2 \text{ c.c.} \end{array}$$

∴ x c.c. of CO_2 yield $2x$ c.c. of CO. ∴ CO produced from CO_2+CO originalyy present $= 2x+(1000-x) = 1600$, where $x = 600$ c.c.

∴ vol. of $CO_2 = 600$ c.c., and the vol. of CO $= 400$ c.c.

4. 10 c.c. of a mixture of CO, CH_4 and N_2 exploded with excess of oxygen, gave a contraction of 6.5 c.c. ; there was a further contraction of 7 c.c. when the gas was treated with KOH. What was the composition of the gas mixture ? *Allahabad* '11.

Let the vol. of CO be x c.c. and that of CH_4 y c.c. ∴ the vol. of $N_2 = (10-x-y)$ c.c. The reactions are :

$$\begin{array}{lccccc} \text{(i)} & 2CO & + & O_2 & = & 2CO_2 & \text{contraction} \\ & 2 \text{ c.c.} & & & & 2 \text{ c.c.} & 1 \text{ c.c.} \\ \text{or} & x \text{ c.c.} & & & & x \text{ c.c.} & x/2 \text{ c.c.} \end{array}$$

$$\begin{array}{lcccccccc} \text{(ii)} & CH_4 & + & 2O_2 & = & CO_2 & + & 2H_2O & \text{contraction} \\ & 1 \text{ c.c.} & & & & 1 \text{ c.c.} & & & 2 \text{ c.c.} \\ \text{or} & y \text{ c.c.} & & & & y \text{ c.c.} & & & 2y \text{ c.c.} \end{array}$$

$\therefore$ the total contraction $= x/2+2y = 6.5$, and total vol. of CO_2 formed $= x+y = 7$. Solving the equations, $x = 5$ and $y = 2$.

$\therefore$ vol. of $CH_4 = 2$ c.c. ; vol. of $CO = 5$ c.c. ; vol. of $N_2 = 3$ c.c.

5. To a mixture of acetylene, hydrogen, and carbon monoxide, occupying 20 c.c., 50 c.c. of oxygen were added and a spark passed. After cooling, the residual gases contained 16 c.c. of carbon dioxide and 36 c.c. of unburnt oxygen. What was the composition of the mixture ?

Let the vol. of C_2H_2 be x c.c. and that of H_2 y c.c. $\therefore$ the volume of $CO = 20-x-y$.

The reactions involved are :

$$\begin{array}{llllll}
\text{(i)} & C_2H_2 & + & 5/2O_2 & = & 2CO_2 \ + \ H_2O. \\
 & 1 \text{ c.c.} & & 5/2 \text{ c.c.} & & 2 \text{ c.c.} \\
\text{or} & x \text{ c.c.} & & 5x/2 \text{ c.c.} & & 2x \text{ c.c.}
\end{array}$$

$$\begin{array}{llllll}
\text{(ii)} & H_2 & + & \frac{1}{2}O_2 & = & H_2O \\
 & 1 \text{ c.c.} & & \frac{1}{2} \text{ c.c.} & & \\
 & y \text{ c.c.} & & y/2 \text{ c.c.} & &
\end{array}$$

$$\begin{array}{llllll}
\text{(iii)} & CO & + & \frac{1}{2}O_2 & = & CO_2 \\
 & 1 \text{ c.c.} & & \frac{1}{2} \text{ c.c.} & & 1 \text{ c.c.} \\
\text{or} & (20-x-y) \text{ c.c.} & & \frac{1}{2}(20-x-y) \text{ c.c.} & & (20-x-y) \text{ c.c.}
\end{array}$$

$\therefore$ carbon dioxide formed $= 2x + (20-x-y) = 16$ or $y-x = 4$

Oxygen used up $= \dfrac{5x}{2} + \dfrac{y}{2} + \dfrac{20-x-y}{2} = 14$, or $4x = 8$. $\therefore$ $x = 2$ and $y = 2$, $\therefore$ composition is 2 c.c. C_2H_2 ; 6 c.c. H_2 ; 12 c.c. CO

6. 20 vols. of a hydrocarbon, mixed with 80 vols. of O_2, gave 60 vols. after explosion and 20 vols. after shaking with KOH solution. What was the gas ?
Calcutta. C_2H_4.

7. 20 c.c. of a hydrocarbon were exploded with 250 c.c. of air. The immediate contraction was 40 c.c. and the volume of CO_2 found by KOH absorption was 20 c.c. What is the composition of the hydrocarbon ? *Calcutta'* 32. CH_4.

8. 40 c.c. of a mixture of CO and C_2H_2 gases were mixed with 100 c.c. O_2 in an eudiometer and fired. After cooling the residual gas occupied 104 c.c. ; and after treatment with KOH the residual gas occupied 48 c.c. Find the composition of the original mixture. *Allahabad* '15. CO 60% ; C_2H_2 40%.

9. 100 c.c. of a mixture of CO, CH_4, and H_2 are mixed with 300 c.c. of O_2 and fired. After cooling the resulting gas occupied 285 c.c. and after absorption by potash 205 c.c. of O_2 remained. Find the composition of the mixture.
CO 50 c.c. ; CH_4 30 c.c. ; H_2 20 c.c. *Calcutta* '41.

10. 15 c.c. of carbon monoxide were mixed with 5 c.c. of oxygen and exploded. What is the volume and composition of the residual gas ? CO 5 c.c.;CO_2 10 c.c.

11. Assuming air contains 21% by volume of oxygen, what volume of air at 27°C and 750 mm. pressure will be required for the complete combustion of 60 gms. of a paraffin candle of 80% carbon and 20% hydrogen ?
Calcutta '35. 831.2 litres.

12. Calculate the percentage composition by volume of a mixture of CO and CH_4, 105.5 c.c. of which required 90.4 c.c. of oxygen for complete combustion.
Calcutta '49. CO 76.2% ; CH_4 23.8%.

23. 5 c.c. of a mixture of methane and ethylene need 13.2 c.c. of oxygen for combustion. Find the volume of each present. 1.8 c.c. CH_4 ; 3.2 c.c. C_2H_4.

Volumetric analysis—Acidimetry and Alkalimetry

Neutralisation.—In neutralisation reactions, acids and bases react with each other in equivalent amounts producing salt and water (p. 90). In the following illustration a measured volume, say 25 c.c., of caustic soda solution is taken in a beaker—a drop of phenolphthalein solution is added to the solution, which is turned *pink* (phenolphthalein is *pink* in alkaline solution, and *colourless* both in neutral and acid solutions). Dilute hydrochloric acid is run into the solution drop by drop from a burette. As each drop of acid mixes with the alkali, the hydrogen ion of the acid reacts with the hydroxyl ion of the alkali, forming water. With the gradual addition of the acid, the hydroxyl ions, therefore, begin decreasing, until at a certain stage all the hydroxyl ions are used up. The solution is then said to be *neutral* and the process is known as *neutralisation.* The solution become *just* colourless at the *neutral point.* The volume of acid is then read from the burette ; let it be 20 c.c.

∴ 25 c.c. of caustic soda solution = 20 c.c. of HCl solution.

Now, knowing the weight of caustic soda per c.c. of the solution, it is possible to calculate the weight of hydrochloric acid per c.c. of its solution from the relation :

$$HCl(36.5) + NaO(40) = NaCl + H_2O.$$

i.e., 36.5 gms. of hydrochloric acid are equivalent to 40 gms. of caustic soda in their power of neutralisation.

Titration.—It is a process of volumetrically determining the unknown strength of a solution by reaction with a solution of known concentration (or what is called a *standard solution*) in presence of an indicator. In acidimetry the unknown strength of an acid solution is estimated by titration with a standard alkali solution. Alkalimetry is just the reverse process.

Let us take an example—25 c.c. of a 5 per cent caustic soda solution just neutralise 20 c.c. of a solution of hydrochloric acid. To find the strength of the acid :

25 c.c. of 5% NaOH solution contain 5/4 gms. of NaOH.

$$\underset{40}{NaOH} + \underset{36.5}{HCl} = NaCl + H_2O.$$

i.e., 40 gms. of NaOH neutralise 36.5 gms. of HCl

∴ 5/4 gms. of NaOH neutralise $(36.5/40) \times 5/4$ or 1.14 gms. of HCl.

∴ 20 c.c. of HCl solution contain 1.14 gms. of HCl.

or 100 c.c. of HCl solution contain 5.7 gms. of HCl.

The strength of the acid is 5.7 per cent. This is an example of acidimetry.

Neutralisation indicator.—An indicator is a substance (a organic acid or base) that has the property of changing colour when acid or base is added to it. When added to a liquid, it indicates by change of colour, if the liquid is acidic, neutral or alkaline; it is invariably used to indicate the end point of neutralisation of acids and alkalis during their titration. A good indicator should show *sharp contrast of colours* in solutions *just* acidic or alkaline. Litmus, methyl orange, methy red, phenolphthalein, etc. are the indicators usually used. Litmus is a dye obtained from certain lichens.

Indicator	Colour in acid	Colour in alkali
Litmus	red	blue
Methyl orange	pink or red	yellow
Methyl red	red	yellow
Phenolphthalein	colourless	pink or red
Congo red	blue	red

Choice of Indicators for neutralisation reactions depends on the strength of acids and bases. HCl, H_2SO_4, HNO_3 are strong acids ; oxalic acid and acetic acid are weak acids. NaOH and KOH are strong alkalis—NH_4OH is a weak base. Na_2CO_3 is the salt of weak carbonic acid.

Titration of :	Indicator
(i) Strong acid—strong base	Any indicator
(ii) Strong acid—weak lase	Methyl orange*
(iii) Weak acid—strong base	Phenolphthalein**

A weak acid is not titrated with a weak base, as no sharp end point is obtained.

* Methyl orange changes colour in fairly acid solution. The salt formed during neutralisation, e.g., $NH_4Cl + H_2O \rightleftharpoons NH_4OH + HCl$, is hydrolysed giving a slightly acidic solution at the equivalence point.

** Phenolphthalein becomes pink in fairly alkaline solution, as the salt formed during neutralisation, e.g.,

$$CH_3COONa + H_2O \rightleftharpoons CH_3COOH + NaOH,$$

is hydrolysed giving an alkaline solution at the end point. Methyl orange is the indicator in the titration of sodium carbonate with a strong acid, since the solution is acidic at the end point due to the displacement of carbonic acid.

$$Na_2CO_3 + 2HCl = 2NaCl + H_2O + CO_2$$

But phenolphthalein becomes colourless (i.e., pink colour of Na_2CO_3 solution disappears) when only *half* of Na_2CO_3 is neutralised—at this stage Na_2CO_3 is converted into $NaHCO_3$ which is not alkaline to phenolphthalein.

$$Na_2CO_3 + HCl = NaHCO_3 + NaCl.$$

Standard solution.—A standard solution of a substance contains a known weight of it in a definite volume of the solution. Hence a standard solution is a solution of known strength, i.e., known concentration. The standard solution usually employed in titrations is the normal solution.

Normal solution.—*A normal solution* of a substance contains one gram-equivalent of it per litre of the solution.

Equivalent weights.—The equivalent weight of an element has already been considered (p. 73). The equivalent weight of a compound is that weight of it which contains one gram equivalent weight of the component taking part in a reaction. With acids, the chief component is the replaceable hydrogen ; with bases, it is the hydroxyl group, and with salts, it is generally the cation.

(i) **The gram equivalent of an acid** *is that weight of it which contains* 1.008 *grams of replaceable hydrogen* i.e. *which contains* 1 *atom of replaceable hydrogen.*

A normal solution is written as *N solution*, e.g. (N)HCl solution. Strengths of other solutions are expressed in terms of N solution ; thus, solutions containing 1/2, 1/10th, 1/100th, twice or thrice the equivalent of a substance per litre are written as N/2 (semi-normal), N/10 (deci-normal), N/100 (centi-normal), 2N (twice normal) or 3N (thrice normal) respectively.

The number of replaceable hydrogen atoms in the molecule of an acid is its basicity (p. 91).

$\therefore$ Gram-equivalent of an acid = its gram-molecular weight $\div$ basicity.

Acid	Mol. wt.	Basicity	Gram. equivalent
Hydrochloric HCl	36.46	1	36.46
Nitric, HNO_3	63	1	63.0
Sulphuric, H_2SO_4	98	2	49
Oxalic acid, $C_2H_2O_4.2H_2O$	126	2	63
Phosphoric, H_3PO_4	98	3	32.67

Since 36.46 gms. of HCl = 22.4 litres of HCl gas at N.T.P., 22.4 litres of HCl at N.T.P. is also the equivalent of HCl.

(ii) **The gram-equivalent of a base** *is that weight of it which can neutralise one gram-equivalent of an acid.* i.e., *which reacts with* 1.008 *gms of replaceable hydrogen of an acid.*

One hydroxyl group reacts with one replaceable hydrogen atom, and hence the equivalent of a hydroxide = its molecular weight divided by the number of hydroxyl groups contained in its molecule.

$$NaOH+HCl = NaCl+H_2O : Ca(OH)_2+2HCl = CaCl_2+2H_2O.$$

One oxygen atom reacts with two hydrogen atoms, and henece the equivalent of a basic oxide = its molecular weight divided by *twice* the number of oxygen atoms contained in its molecule.

$$MgO + 2HCl = MgCl_2 + H_2O ; \quad Al_2O_3 + 6HCl = 2AlCl_3 + 3H_2O.$$

The number of gram-equivalents of an acid which neutralises one gram-molecular weight of a base is the *acidity* (p. 98) of the base.

∴ Gram-equivalent of a base = its gram-molecular weight ÷ acidity.

Base	Mol. wt.	Basicity	Gram equivalent
Caustic soda, NaOH	40	1	40
Caustic potash, KOH	56	1	56
Calcium hydroxide, $Ca(OH)_2$	74	2	37
Ammonia, NH_3	17	1	17
Ferric oxile, Fe_2O_3	160	6	26.67
Ferric hydroxide, $Fe(OH)_3$	107	3	35.67

17 gms. of NH_3 = 22.4 litres of NH_3 at N.T.P. = equivalent of NH_3.

(iii) **The gram-equivalent of a normal salt** *is that weight of it which contains one gram-equivalent of a metal* (*which is equivalent to* 1.008 *grams of hydrogen*). Since the gram-equivalent of a metal is the atomic weight divided by the valency, the equivalent of salt=its molecular weight divided by the *total valency* of the metal atoms contained in a molecule, i.e.,

$$\text{Gram-equivalent of a salt} = \frac{\text{gram molecular weight}}{\text{number of metal atoms} \times \text{its valency}}$$

Salt	Mol. wt.	Total valency of metal	Eq. wt.
Sodium carbonate, Na_2CO_3	106	2	53
Calcium carbonate, $CaCO_3$	100	2	50
Ferric chloride, $FeCl_3,6H_2O$	270.5	3	90.17
Silver nitrate, $AgNO_3$	170	1	170
Silver chloride, AgCl	143.34	1	143.34
Copper Sulphate Cu SO_4 $.5H_2O$	249.5	2	124.75

In the case of salts which react with acids, such as carbonate, equivalents may also be determined with reference to the acids. The equivalent of the salt = its molecular weight divided by the number of equivalents of an acid with which one molecule of the salt reacts : thus,

$$Na_2CO_3+2HCl = 2NaCl+H_2O+CO_2$$

One molecule of Na_2CO_3 reacts with 2 equivalents of HCl, and hence the equivalent of Na_2CO_3 = its mol. wt.÷2 = 106÷2 = 53.

The equivalent weight of sodium bicarbonate, $NaHCO_3$, is it molecular weight which is 84, since it reacts with one equivalent of an acid :

$$NaHCO_3 + HCl = NaCl + H_2O + CO_2.$$

The equivalent of a compound, in general, is that weight of it which reacts with one equivalent of an element or compound whose equivalent is known ; thus in $2NaOH + CO_2 = Na_2CO_3 + H_2O$.
2 equivalents of NaOH react with one molecule of CO_2.

∴ 1 equivalent of NaOH reacts with ½ molecule of CO_2.

∴ the equivalent of CO_2 = mol. wt./2 = 44/2 = 22.

In must be clearly understood that the equivalent weight of a substance will depend upon the particular reaction in which it takes part.

A molar solution of a substance contains one gram-molecular weight (or one mole) of it per litre of the solution ; thus a molar solution of H_2SO_4 contains 98 gms. of it per litre, but is normal solution contains only 49 gms. per litre.

Important principles in volumetric analysis.—(i) *Normality of a solution is equal to the number of gram equivalents of a solute per litre*, e.g., the normality of 0.4N NaOH solution is 0.4.

(a) $\text{Normality} = \dfrac{\text{weight of solute in grams per litre}}{\text{gram equivalent}}$

∴ (b) Weight of solute in gram per litre = normality × gram equivalent.

Thus, the weight of NaOH per litre of a 1.5N caustic soda solution = 1.5×40 = 60 gms.

Strength of a solution is usually expressed in terms of *normality* or *weight in gram per litre*, and sometimes in *percent strength*, e.g. a 2 p.c. NaOH solution means 2 gms. of NaOH per 100 c.c. or 10×2 gms., i.e. 10×per cent strength per litre, and hence :

(c) $\text{Normality} = \dfrac{10 \times \text{per cent strength}}{\text{gram equivalent}}$

Thus normality of a 8 p.c. NaOH solution $= 10 \times 8/40 = 2$N.

(ii) *Volume of a given solution is inversely proportional to its strength*, i.e., if the volume be increased the strength must be proportionately decreased, and *vice versa*.

Let the equivalent weight of a solute be p gms.

1000 c.c. of N solution of the solute contains p gms. of it.

or 1 c.c. of the N solution of the solute contain $0.001 \times p$ gm.

or $x.y$ c.c. of the N solution of the solute contains $0.001 \times p \times xy$ gms.

Also, 1 c.c. of y (N) solution of the solute contains $0.001 \times py$ gms.

$\therefore$ x c.c. of y (N) solution of the solute contains $0.001 \times p \times xy$ gms.

$\therefore$ x c.c. of y (N) solution $= xy$ c.c. of (N) solution $= 0.001 \times p \times xy$ gm. of solute.

i.e., **x c.c. of a y (N) solution = xy c.c. of a (N) solution.**

(iii) *One equivalent of any acid can neutralise one equivalent of any base. Hence, solutions of acids and bases of the same strength must neutralise in equal volumes.*

Let x c.c. of a y (N) acid solution neutralise p c.c. of a q (N) base solution.

Now, x c.c. y (N) acid solution $= xy$ c.c. of (N) acid solution
p *c.c.* of q (N) base solution $= pq$ c.c. of (N) base solution.

Since solutions of the *same* strength react in *equal* volumes xy *c.c.* must be equal to pq c.c.

i.e., **volume of an acid × its strength = vol. of a base × its strength**

For two solutions which are equivalent :
volume × strength (solution I) = volume × strength (solution II).

(iv) **Reduction of strength by dilution.**—When a solution is *stronger* than the desired strength, it may be reduced to required strength by proper dilution.

Reduce to N/10 two hundred fifty (250) c.c. of 1.048 N/10 NaOH solution.

250 c.c. of 1.048 N/10 solution $= 250 \times 1.048$ c.c. of N/10 solution.
$= 262$ c.c. of N/10 solution.

$\therefore$ to reduce the strength to *exactly* N/10 $(262-250)$ or 12 c.c. of water are to be added to 250 c.c of the solution.

Preparation of standard solution.—(i) **To prepare 250 c.c. of N/10 sodium carbonate solution.**—The gram equivalent of Na_2CO_3 is 53 gms., hence the requirement for 1 litre of N/10 solution $= 5.3$ gms., and that for 250 c.c. of N/10 solution $= 5.3 \div 4 = 1.325$ gms.

Some *pure* and *dry* sodium carbonate is taken in a weighing bottle ; and about 1.325 gms. of it are *accurately weighed* out into a measuring flask of 250 c.c. capacity with the help of a chemical balance, and dissolved with distilled water—the volume of the solution is then made up to *just* 250 c.c. by gradual addition of water. The contents of the flask is well shaken to get a uniform solution.

Let the amount of sodium carbonate *actually* weighed = 1.3568 gms.

Now, 1.325 gms. per 250 c.c. of solution make just N/10 solution.

∴ 1.3568 gms. per 250 c.c. make (1.3568/1.325) N/10, i.e., 1.024 N/10 solution ; 1.024 is called the *factor* of the solution.

Now, 250 c.c. of 1.024 N/10 Na_2CO_3 solution = 250 × 1.024 or 256 c.c. N/10 Na_2CO_3 solution.

Hence (256−250) or 6 c.c. of water are to be added to the solution to make it *exactly* N/10.

Factor.—Factor of a solution = weight *actually dissolved* ÷ the *theoretical weight* required to be dissolved to prepare a solution of given strength.

In the above example, 1.024 is the factor of the N/10 Na_2CO_3 solution ; and hence the strength of the solution = 1.024 N/10.

The strength of a given solution is usually expressed with a factor.

(i) **To prepare approximately N/10 solution of sulphuric acid.**—The equivalent of sulphuric acid is 49 gms. and hence 1 litre of the N/10 solution will contain 4·9 gms. of the acid. But sulphuric acid is not weighed, since it is *highly hygroscopic* and is also *not cent per cent pure.* From the specific gravity and the purity of a sample of acid, the volume of it that will contain 4.9 gms. of real and *pure* sulphuric acid is calculated.

Let the specific gravity of a sample of sulphuric acid be 1.84 and its purity 95.6 per cent.

95.6 gms of pure H_2SO_4 are present in 100 gms. of the sample of the acid.

∴ 4.9 gms. of ,, ,, ,, ,, ,, (100 × 4.9)/95.6 gm. of the acid.

Now, mass = volume × density ; and hence the volume of the sample of acid required = weight of the acid divided by its density = (100 × 4.9/95.6) ÷ 1.84 = 2.8 c.c nearly. Hence, about 2.8 c.c. of the sample of the acid is measured out by a pipette into a litre-measuring flask and diluted with water up to 1000 c.c. This is approximately N/10 sulphuric acid solution. Similarly, approximately standard solutions of HCl and HNO_3 can be prepared.

To prepare 1 litre of an approximately (N) acid solution.

Let *e* = *equivalent weight of acid.*

p = purity, i.e., per cent strength by weight.

s = sp. gr. of a sample of acid.

v = volume of the acid to be diluted to 1 litre.

The, $v = 100\ e/ps$.

Some typical volumetric analysis.—(i) **To find the strength of an acid solution** i.e., standardisation of an acid solution. The strength of an acid solution is determined by titration against a standard solution of sodium carbonate which is directly prepared, since the sodium carbonate can be obtained very pure and accurately weighed easily. N/10 solutions are usually used in volumetric analysis.

A burette (fig. 85) is filled with the approximately N/10 sulphuric acid solution up to the zero mark. 25 cc. of N/10 sodium carbonate solution is taken in a basin by means of a pipette and diluted to about 50 c.c. with water—a drop of *methyl orange* solution (indicator) being added to the solution, which turns the solution *yellow*.

The acid solution is gradually added drop by drop from the burette to the sodium carbonate solution until the *pink colour* is just obtained—the solution being carefully stirred with a glass rod during the titration. The volume of the acid used up is read from the burette. Three titrations are usually done and the mean of three readings taken. Suppose

25 c.c. 1.024 N/10 Na_2CO_3 solution = 24 c.c. acid solution.

Let x = the strength of the acid solution.

$\therefore$ $24 \times x = 25 \times 1.024$ (N/10), whence $x = 1.067$ (N/10).

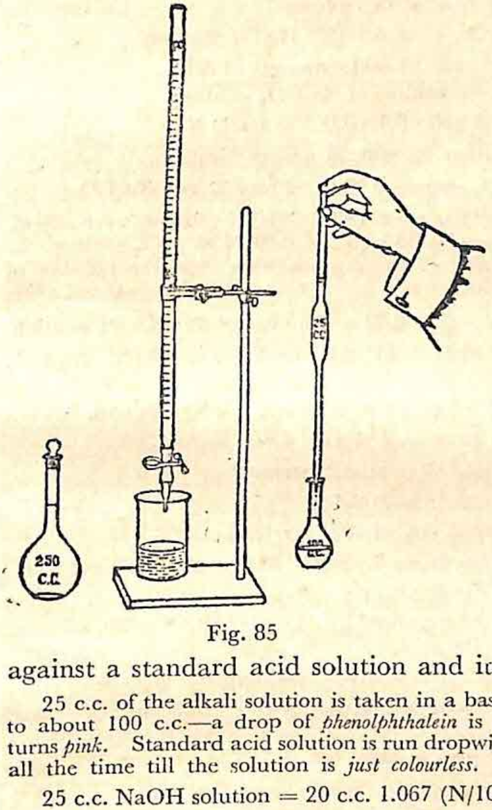


Fig. 85

(ii) **To prepare approximately N/10 caustic soda solution** and determine its strength. Since caustic soda is hygroscopic, its standard solution cannot be prepared by weighing only. Equivalent weight of caustic soda is 40 gms. ; and hence a deci-normal solution will contain 4 gms. of caustic soda per litre.

Approximately N/10 solution is prepared by dissolving about 4 gms. of caustic soda (usually a slight excess is used, since caustic soda is not generally of cent percent purity), obtained by weighing in a rough balance, in a litre of water. The solution is then titrated against a standard acid solution and its strength determined.

25 c.c. of the alkali solution is taken in a basin by means of a pipette and diluted to about 100 c.c.—a drop of *phenolphthalein* is added to the solution ; the solution turns *pink*. Standard acid solution is run dropwise from a burette, stirring the solution all the time till the solution is *just colourless*. Suppose :

25 c.c. NaOH solution = 20 c.c. 1.067 (N/10) acid solution.

$\therefore$ strength of NaOH solution = (20 × 1.067/25).N/10 = 0.8536 (N/10).

Exercises

1. What weight of sodium carbonate is required to neutralise 50 c.c. of normal H_2SO_4 ? *Calcutta* '13.

50 c.c. of N.H_2SO_4 will be neutralised by 50 c.c. of N.Na_2CO_3 solution.

Now, 1000 c.c. of (N) Na_2CO_3 solution contain 53 gm. of Na_2CO_3.

$\therefore$ 50 c.c. ,, ,, ,, ,, 2.65 gm. of Na_2CO_3.

2. 25 c.c. of N/10 hydrochloric acid neutralised 21 c.c. of solution of sodium carbonate. How much water must be added to 1 litre of the latter in order to make it exactly decinormal ?

21 c.c. of Na_2CO_3 solution = 25 c.c. of N/10 HCl solution.

∴ strength of Na_2CO_3 solution = (25/21) N/10 = 1.1905 (N/10).

∴ 1000 c.c. of 1.1905 (N/10) Na_2CO_3 solution = 1000×1.1905 or 1190.5 c.c. of (N/10) Na_2CO_3 solution.

∴ (1190.5 − 1000) or 190.5 c.c. of water are to be added to 1000 c.c. of the solution.

3. 20 c.c. of a N/10 solution of HNO_3 is neutralised by 22.5 c.c. of Na_2CO_3 solution. Calculate the strength of the carbonate solution in terms of normality and the weight of the carbonate per litre of the solution. *Calcutta* '16.

22.5 c.c. of Na_2CO_3 solution = 20 c.c. of 0.1 (N) HNO_3 solution.

$$\therefore \text{ Strength of } Na_2CO_3 \text{ solution} = \frac{\text{vol. of acid} \times \text{strength of acid}}{\text{volume of } Na_2CO_3 \text{ solution}}$$

$$= (20 \times 0.1\text{N})/22.5 = 0.089 \text{ N}$$

Now, 1000 c.c. (N) Na_2CO_3 solution contain 53 gm. of Na_2CO_3.

∴ 1000 c.c. of 0.089 (N) Na_2CO_3 contain 0.089×53 or 4.72 gm. Na_2CO_3.

4. To 50 c.c. of solution of HCl 25 c.c. of 0.82 N.NaOH solution were added. The excess of acid in the solution required 30 c.c. of 0.09 N.Na_2CO_3 solution for neutralisation. Required the normality of the acid solution, and the number of grams of HCl per litre of the solution. *Calcutta* '21.

25 c.c. of 0.82 (N) NaOH solution = 25×0.82 or 20.5 c.c. of (N) NaOH solution.

30 c.c. of 0.09 (N) Na_2CO_3 solution = 30×0.09 or 2.7 c.c. of (N) Na_2CO_3 solution.

Hence the mixture of alkalis = (20.5 + 2.7) or 23.2 c.c. of (N) solution.

Let the strength of HCl solution be x, and since

Volume of acid × its strength = vol. of alkali × its strength

$$\therefore \; 50 \times x = 23.2 \text{ N} \qquad \therefore \; x = 0.464 \text{ N}$$

Now, (N) HCl solution contains 36.5 gm. of HCl per litre.

∴ 0.464 (N) HCl solution contains 36.5×0.464 or 16.93 gms. of HCl per litre.

5. 2.95 gm. of a dibasic acid was dissolved in water and the solution diluted to 250 c.c.; 25 c.c. of this solution was neutralised by 25 c.c. of N/5 Na_2CO_3 solution. Calculate the eq. wt. and mol. wt. of the acid.

25 c.c. of diluted acid = 25 c.c. N/5 Na_2CO_3 solution.

∴ 250 c.c. of diluted acid = 50 c.c. N Na_2CO_3 solution = 50 c.c. of N acid solution.

∴ 50 c.c. N acid contain 2.95 gm. of acid.

or 1000 c.c. N acid contain 59 gm. of acid.

∴ eq. wt. of the acid = gm. and mol. wt. = $59 \times 2 = 118$ gm.

6. A specimen of limestone contains 60% $CaCO_3$. Calculate the amount of stone which will be required to generate just sufficient CO_2 to convert 1 litre of N.NaOH solution into sodium carbonate. *Calcutta* '31.

1 litre of N.NaOH solution contains 40 gms. of NaOH.

$$\underset{80}{2NaOH} + \underset{44}{CO_2} = Na_2CO_3 + H_2O$$

i.e., 80 grms. of NaOH react with 44 gms. of CO_2
40 ,, ,, ,, ,, ,, 22 ,, ,,

$$\text{Now, } \underset{100}{CaCO_3} = CaO + \underset{44}{CO_2}$$

i.e., 44 grms. of CO_2 are obtained from 100 grms. of $CaCO_3$.

∴ 22 gms. ,, ,, ,, ,, 50 gms. ,, ,,

But limestone contains only 60% $CaCO_3$; hence 50 gms. of $CaCO_3$ are present in $(100 \times 50)/60$ or 83.3 gms. of limestone. ∴ limestone required = 83.3 gms.

7. 100 gms. of hydrochloric acid solution of sp. gr. 1.17 contain 33.4 gm. HCl. How many litres of acid solution of this strength would be required to neutralise 5 litres of a solution of caustic soda containing 0.042 gm. of NaOH per c.c. ?

1 c.c. of NaOH solution contains 0.042 gm. NaOH.

∴ 5 litres ,, ,, ,, 0.042×5000 or 210 gm. NaOH.

$$\text{Now,}\quad \underset{40}{NaOH} + \underset{36.5}{HCl} = NaCl + H_2O$$

i.e., 40 gms. NaOH neutralise 36.5 gms. of HCl.

∴ 210 gms. ,, ,, 191.625 gm. of HCl

But only 33.4 gm. of HCl are present in 100 gm. of HCl solution.

∴ 191.625 gm. HCl are present in 573.7 gm. HCl solution.

Now, since mass = volume × density, the volume of HCl solution required $= 573.7 \div 1.17 = 490$ c.c. or 0.49 litre.

8. A weighed amount of ammonium chloride was boiled with an excess of strong caustic soda solution and the liberated gas was absorbed by 100 c.c. of a solution containing 4.9 gm. of H_2SO_4 ; part of the acid was thus neutralised, and the excess acid could be neutralised by 50 c.c. of sodium carbonate solution containing 2.65 gm. of Na_2CO_3. Calculate the amount of ammonium chloride originally taken.

Normality of a solution = wt. of the solute per litre/the eq. wt.

∴ strength of the H_2SO_4 solution $= 4.9 \times 10/49 = 1N$.

Strength of the Na_2CO_3 solution $= 2.65 \times 20/53 = 1N$.

50 c.c. $N.Na_2CO_3$ solution = 50 c.c. $N.H_2SO_4$ solution.

∴ (100 − 50) or 50 c.c. N.acid were used in absorbing NH_3.

Now, 50 c.c. N.acid solution = 50 c.c. $N.NH_3$ solution.

= 50 c.c. $N.NH_4Cl$ solution.

$$NH_4Cl + NaOH = NaCl + H_2O + NH_3.$$

The eq. wt. of NH_4Cl = its mol. wt. = 53.5 gm.

∴ wt. of NH_4Cl originally taken $= 50 \times 0.0535$ gm. = 2.675 gm.

9. 1.08 g. of NH_4Cl was boiled with 62 c.c. of (N/2) NaOH till free from ammonia. 44 c.c. of N/4 HCl were required for neutralising the excess of alkali in the mixture. Calculate percentage of ammonia in the salt. *Calcutta* 1935.

62 c.c. (N/2) NaOH solution = 31 c.c. (N) NaOH solution.

Excess alkali = 44 c.c. (N/4) HCl = 11 c.c. (N) HCl.

= 11 c.c. (N) NaOH solution.

∴ (31 − 11) or 20 c.c. (N) NaOH were used to displace NH_3.

20 c.c. (N) NaOH = 20 c.c. (N) NH_3 $= 20 \times 0.017$ gm. NH_3.

$$\therefore\ \text{p.c. of } NH_3 \text{ in } NH_4Cl = \frac{20 \times 0.017 \times 100}{1.08} = 31.48.$$

10. One gram of impure sodium carbonate is dissolved in water and the solution is made up to 250 c.c. To 50 c.c. of this solution 30.4 c.c. of 0.15 (N) HCl is added and the mixture requires for neutralising 10 c.c. of 0.12 (N) NaOH solution. Determine the strength of impure Na_2CO_3 solution in terms of normality and also the % of pure sodium carbonate in the impure sample. *Calcutta* '23.

30.4 c.c. of 0.15 (N) HCl solution $= 30.4 \times 0.15$ or 4.56 c.c. of (N) HCl.

10 c.c. of 0.12 (N) NaOH solution = 1.2 c.c. of (N) NaOH solution.

= 1·2 c.c. of (N) HCl solution.

Hence (4.56 − 1.2) or 3.36 c.c. of (N) HCl solution neutralise 50 c.c. of the sodium carbonate solution.

Let x be the strength of the Na_2CO_3 solution, then

$50x = 3.36N$ whence $x = 0.0672N$.

1 c.c. of (N) Na_2CO_3 solution contains 0.053 gm. Na_2CO_3.

∴ 1 c.c. of 0.0672N solution contains 0.053×0.0672 gm. Na_2CO_3.

∴ 250 c.c. of 0.0672 N solution contains $0.053 \times 0.0672 \times 250$ or 0.8904 gm. Na_2CO_3. Hence, 1 gm. impure Na_2CO_3 contains 0.8904 gm. pure Na_2CO_3.

∴ 100 gms. impure Na_2CO_3 contains 89.04 gm. pure Na_2CO_3.

∴ % of Na_2CO_3 in the impure sample = 89.04.

11. 584 c.c. of gaseous hydrochloric acid measured at N.T.P. were passed into a solution of KOH. After the reaction the solution still remained alkaline. To this was added 58 c.c. of 1.2N H_2SO_4 when the solution was completely neutralised. Calculate the total quantity of alkali in the solution. *Calcutta* ' 40

22400 c.c. of HCl gas at N.T.P. = 1000 c.c. of (N) HCl solution.

∴ 584 c.c. of HCl gas at N.T.P. = 26 c.c. of (N) HCl solution.

Hence, the KOH soln. = 26 c.c. of (N) HCl + 58 c.c. of 1.2 (N) H_2SO_4.
= 26 c.c. of (N) HCl + 69.6 c.c. of (N) H_2SO_4.
= (26 + 69.6) or 95.6 c.c. of (N) acid solution.
= 95.6 c.c. of (N) KOH solution.

Now, 1 c.c. of (N) KOH solution contains 0.056 gm. KOH.

∴ 95.6 c.c. of (N) KOH solution contains 95.6×0.056 or 5.3536 gm. KOH.

∴ total alkali in the solution = 5.3536 gm.

12. 1.5 gms. of a mixture of sodium carbonate and bicarbonate were dissolved in 250 c.c. of water. 25 c.c. of the solution required 27 c.c. of (N/10) HCl for neutralisation. Find the composition of the mixture.

25 c.c of the mixture = 27 c.c. N/10 HCl solution.

∴ 250 c.c. of the mixture = 27 c.c. NHCl solution.

Let the $NaHCO_3$ be x gm. ∴ the $Na_2CO_3 = (1.5-x)$ gm.

$NaHCO_3 + HCl = NaCl + H_2O + CO_2$.

84 gm. 36.5 gm. or 1000 c.c. NHCl solution.

∴ x gm. of $NaHCO_3 = 1000x/84$ c.c. NHCl solution.

$Na_2CO_3 + 2HCl = 2NaCl + H_2O + CO_2$.

106 gm. 2×36.5 or 2000 c.c. NHCl solution.

∴ $(1.5-x)$ gm. of $Na_2CO_3 = 1000\,(1.5-x)/53$ c.c. NHCl solution.

∴ total acid required $= 1000x/84 + 1000\,(1.5-x)/53$.

∴ $1000x/84 + 1000\,(1.5-x)/53 = 27$; whence $x = 0.187$, etc.

∴ $NaHCO_3 = 0.187$ gm. and $Na_2CO_3 = 1.313$ gm.

13. 0.02 gm. of a metal after solution in water produced an alkali which was neutralised by 10 c.c. of N/10 HCl solution. Find the eq. wt. of the metal.

10 c.c. N/10 HCl solution = 0.02 gm. of metal.

i.e., 1 c.c. NHCl solution = 0.02 gm. of metal.

∴ 1000 c.c. NHCl solution = 20 gm. of metal.

∴ equivalent weight of the metal = 20.

14. 0.1232 gm. of a metal was dissolved in 50 c.c. N/2 HCl and the solution diluted to 100 c.c. ; 20 c.c. of this solution was neutralised by 30 c.c. N/10 caustic soda. Calculate the eq. wt. of the metal.

20 c.c. diluted acid = 30 c.c. N/10 caustic soda.

∴ 100 c.c. diluted acid = 15 c.c. N caustic soda.
= 15 c.c. NHCl which was left unused.

Vol. of acid taken = 50 c.c. N/2 HCl. = 25 c.c. NHCl.

∴ Vol. of acid reacting with the metal = (25−15) or 10 c.c. NHCl.

i.e., 10 c.c. NHCl react with 0.1232 gm. of metal.

∴ 1000 c.c. NHCl react with 12.32 gm. of metal.

∴ eq. wt. of metal = 12.32.

Exercises 13 *and* 14 *illustrate methods of finding eq. wts. of metals by titration.*

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15. 55 c.c. of NaOH solution require 41 c.c. normal H_2SO_4 to neutralise it. Calculate the strength of alkali solution in terms of (a) normality, (b) percentage. *Andhra* 1934. (a) 0.7454 N. (b) 2.98%.

16. 1.3456 gm. of Na_2CO_3 are dissolved in water and the volume of the solution made up to 250 c.c. 25 c.c. of this solution exactly neutralised 24.85 c.c. of a solution of H_2SO_4. Calculate the normality of (a) Na_2CO_3 solution, (b) acid solution, and the amount of Na_2SO_4 formed on neutralisation. *Calcutta* '53. (a) 0.1016 N. (b) 0.1022 N ; Na_2SO_4 0.1803 gm.

17. What weight of anhydrous sodium carbonate would be needed to prepare 500 c.c. of N/10 sodium carbonate solution ? 2.65 gm.

18. In preparing a N/10 caustic soda solution about 4.4 gm. were weighed out and made up to 1 litre. 20 c.c. of this solution were neutralised by 22.2 c.c. N/10 HCl. How much water must be added to 250 c.c. of this caustic soda solution to make it exactly N/10 ? 27.5 c.c.

19. 5.3 gms. of moist sodium carbonate require 90 c.c. of a normal solution of acid to neutralise it. What is the percentage of water ? 10 per cent.

20. The specific gravity of pure nitric acid is 1.522. What volume of such acid would be required to just neutralise 100 gms. of KOH ? 73.9 c.c.

21. 22 c.c. of N/2 H_2SO_4 neutralised 20.6 c.c. of KOH solution. How much water must be added to 1 litre of the latter to make it exactly N/2 ? 68 c.c.

22. 0.4 g. of pure calcium carbonate was found to require 45 c.c. of dilute HCl for neutralisation. Calculate the normality of the acid. *Punjab* 1942. 0.1778 N.

23. 2.25 gm. of a dibasic acid was dissolved in water and the solution diluted to 250 c.c. 25 c.c. of this solution required 40 c.c. of 1.25 N/10 alkali for neutralisation. Calculate the equivalent and molecular weights of the acid. Eq. wt. 45 ; mol. wt. 90.

24. What volume of normal sulphuric acid would be required to neutralise 5 litres of ammonia at 27°C and 750 mm. pressure ? 2 litres.

25. 1.125 gm. of an acid (mol. wt. 90) was dissolved in 250 c.c. water ; 25 c.c. of the solution were neutralised by 25 c.c. N/10 Na_2CO_3 solution. Find the eq. wt. and basicity of the acid. Eq. wt. 45 ; basicity 2.

26. What do you understand by a standard solution ? How can you prepare a deci-normal solution of sulphuric acid ?

Equal weights of NaOH and KOH are taken. Explain which would neutralise the larger quantity of an acid. Caustic soda.

27. What is meant by neutralisation ? Why is a solution of sodium carbonate alkaline ? Why must phenolphthalein not be used as an indicator for titration with sodium carbonate ?

10 gms. of soda crystals ($Na_2CO_3,10H_2O$) are required to neutralise 50 c.c. of sample of HCl solution. How many c.c. of this acid must be diluted and made up to one litre so that we may get a N solution of HCl ? *Calcutta* '20. 715 c.c.

28. What volume of pure NH_3 at 27° and 750 mm. would be obtained from 10 gms. of NH_4Cl ? What volume of N/10 H_2SO_4 would be neutralised by this ammonia. *Calcutta* '19. 4.661. ; 1.87 litres.

29. 25 c.c. of an alkali solution is mixed with 8 c.c. of a 0.75 (N) acid solution and for complete neutralisation it further required 15 c.c. of a 0.8 N acid solution. Find the strength of the given alkali solution. *Calcutta* '30. 0.72 N.

30. 1.524 gms. of ammonium chloride were dissolved in water and 50 c.c. of (N) KOH solution were added to it. The total solution was boiled till ammonia ceases to be evolved, and was then neutralised with 30.95 c.c. (N) H_2SO_4 solution. Calculate the percentage of ammonia in the sample of ammonium chloride. *Calcutta* '31. 21.25%.

31. 0.3363 gm. of a metal when added to 73 c.c. of distilled water produced 190 c.c. of hydrogen at 27°C and 720 m.m. and the solution became alkaline. Calculate the equivalent weight of the metal and the strength of the alkaline solution in terms of normality. Guess what the metal is. 1*l*. of hydrogen at N.T.P. weighs 0.089 gm. Eq. wt. 23 ; 0.2 N ; sodium. *Calcutta* '52.

31a. What volume of N/10 HCl would completely dissolve 50 gms. of calcium carbonate. 10 litres.

32. Concentrated hydrochloric acid has a specific gravity 1.16 and contains 32 per cent of hydrogen chloride. Calculate the volume of this liquid which would be required to make ten litres of a normal solution of this acid. *Gauhati* '52 ; 983.3 c.c.

33. 25 c.c. of NaOH solution exactly neutralises 22.5 c.c. of a solution (containing 1.4175 gm. in 250 c.c.) of a dibasic acid the molecular weight of which is 126, and 10 c.c. of the same NaOH solution also exactly neutralises 8 c.c. of a solution of H_2SO_4. Calculate the strength of the H_2SO_4 solution. *Calcutta* '29. 0.1013N..

34. 1 gm. of a mixture of sodium carbonate and bicarbonate was dissolved in 250 c.c. water. 25 c.c. of the solution required 15 c.c. of N/10 HCl for neutralisation. Find the percentage composition of the mixture. Na_2CO_3 44·45% ; $NaHCO_3$ 55·55%

35. 1.216 gm. of ammonium sulphate were boiled with an excess of caustic soda and the ammonia collected in 100 c.c. N.H_2SO_4. The partly neutralised acid was then titrated with N.NaOH solution and it required 81.6 c.c. of this solution to reach the end point. Calculate the percentage of ammonia in ammonium sulphate. *Punjub* '35; 25·72,

36. 16 gm. of a mixture of sodium sulphate and bisulphate was made up to 250 c.c. 10 c.c. of this require for neutralisation 8.4 c.c. of N/2 NaOH. Calculate the amount of sodium bisulphate. 12.6 gm.

37. 3.12 gm. of washing soda crystals were dissolved in 200 c.c. of water. 20 c.c. of the resulting solution required 21.8 c.c. of N/10 H_2SO_4 for exact neutralisation. Calculate the percentage weight of anhydrous sodium carbonate in the crystals. 37.02.

38. 4.35 gms. of a mixture of NaCl and anhydrous Na_2CO_3 were dissolved in water and the solution made up to 100 c.c. 20 c.c. of the solution required 15.5 c.c. of N/2 H_2SO_4 to react completely with the sodium carbonate. Calculate the percentage composition of the original mixture. NaCl, 52.8% ; Na_2CO_3. 47.2%.

38a. 0.12 gm. of a metal dissolved completely in 25 c.c. N/2 HCl solution ; the excess acid required 25 c.c. N/10 NaOH solution for neutralisation. Find the eq. wt. of the metal. 12.

39. 1.054 gm. of a carbonate of a bivalent metal is dissolved in 50 c.c. N HCl and the excess of acid is neutralised by 25 c.c. N caustic soda. Find the eq. wt. and the at. wt. of the metal. Eq. wt. 12.16 ; at. wt. 24.32.

40. 0.21 gm. of a metal was treated with 100 c.c. N/2 H_2SO_4 till the metal dissolved completely. The residue required 32.5 c.c. of (N) NaOH solution for neutralisation. Calculate the equivalent of the metal. *Rajputana* '52. 12.

41. 20 c.c. of a solution of H_2SO_4 neutralises 21.2 c.c. of a 3 per cent solution of Na_2CO_3. How would you reduce the strength of the acid to decinormal ?

Strength = 0.6 N. To every 1 c.c. of solution 5 c.c. of water.

42. Explain what do you understand by the normality of an acid or base. What is meant by neutralisation ?

25 c.c. of solution of sulphuric acid neutralise 22.5 c.c.'s of a 4 per cent solution of sodium carbonate. How would you reduce the strength of the acid to decinormal ? *Calcutta* '48. 1 litre to be diluted to 6.79 litres.

43. 7.5 g. of a dibasic acid are dissolved in water and the volume made up to 250 c.c. 25 c.c. of this acid solution require 16.1 c.c. of N NaOH for neutralisation. Find the molecular weight of the acid. 93.17.

44. Explain what is meant by a normal solution. How does it differ from a 'molar' solution of a substance ? What weight of sodium carbonate, sodium bicarbonate and sulphuric acid will be required to prepare a normal solution of each ?

An excess of ferrous sulphide is added to 125 c.c. of dilute sulphuric acid and the volume of hydrogen sulphide set free measured 560 c.c. at 0°C and 760 m.m. Calculate the normality of the acid. *Calcutta* '49. 0.4 N.

45. 2 gms. of the carbonate of a metal were dissolved in 50 c.c. (N) HCl solution. The resulting liquid required 100 c.c. N/10 NaOH solution to neutralise it completely. Calculate the equivalent weight of the carbonate. *Rajputana*, '53. Ans. 50.

46. 10 c.c. of N sodium carbonate was required to neutralise 20 c.c. of a solution of sulphuric acid. What volume of gas would be obtained at N.T.P. by the action of 100 c.c. of this acid on zinc ? *Calcutta* 1959 ; 0.56 litre.

47. 0.125 g. of sodium carbonate was dissolved in water and it was found that 24.8 c.c. of a solution of sulphuric acid were required to neutralise it exactly. Calculate (a) the normality of the acid, (b) the weight of sulphuric acid present in one litre. *P. U.* (*Cal.*), 1961. *Ans.* (a) 0.0951 N ; (b) 4.66 gm.

XXIV

ORGANIC CHEMISTRY

INTRODUCTION

The growth of organic Chemistry.—Numerous natural products of plant or animal, e.g., oils, fats, sugars, starch, etc., had been known to the ancient people. Such common things as soap, dyes, drugs, wine, beer, perfumes and poisons, have been made since early times. The art of dyeing with indigo and alizarin is also a very old practice.

The next phase is marked by the isolation of many individual compounds. *Alcohol* was obtained very early by distillation of wine, and so also *acetic acid* by distillation of vinegar. Many acids were isolated from fruit and animal juices. *Formic acid* was prepared by distilling red ants. Towards the end of the 18th century Scheele isolated *citric acid* from lemon, *lactic acid* from sour milk, *oxalic acid* from wood sorrel, *gallic acid* from nut galls, *benzoic acid* from gum benzoin, and *tartaric acid* as the sour principle of grapes. He also isolated *glycerine* from olive oil. In 1773 Rouelle isolated *urea* from human urine. *Morphine* was isolated from opium in 1805. The early chemists of the period also isolated the drugs *quinine*, *cinchonine* and *strychnine*.

These and similar natural products were called **organic** to denote their origin from plant or animal sources, and were thus distinguished from inorganic substances such as acids, bases and salts, etc., which are made from lifeless rocks and minerals.

But beyond the separation of a number of natural products, nothing was known about their chemical nature. In 1874 Lavoisier showed by combustion analysis that *all* organic compounds consisted of *at least* carbon and hydrogen (hydrocarbons) and frequently oxygen (alcohol) and nitrogen (urea, morphine). Most of the organic compounds of diverse types and properties were soon found to be made of a few elements only, namely carbon, hydrogen, oxygen and nitrogen. Substances so unlike in properties as alcohol, acetic acid, sugar, oils and glycerine, are made up of the *same* three elements carbon, hydrogen and oxygen in different proportions.

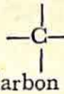
This was in sharp contrast to the inorganic compounds which were distinguished by their simplicity in composition. It was argued that such complexity in composition in organic compounds could be evolved out of a few elements only through the operation of a mysterious force *inherent in living cells*; this was called **vital force.** This led Berzelius to believe that organic compounds were produced under the influence of vital force, and that they could not be prepared artificailly. Organic substances could only be isolated as products of life processes.

This barrier of *vital force* which separated organic from inorganic chemistry was broken down in 1828, the year Wohler artificially prepared urea, a product of animal origin, by evaporating an aqueous solution of ammonium cyanate, an inorganic salt:

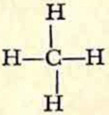
$$NH_4CNO \text{ (ammonium cyanate)} = CO(NH_2)_2 \text{ (urea)}$$

This was a direct refutation of the vital force theory. The synthesis of urea was followed by others, e.g., synthesis of acetic acid, and so the belief in vital force disappeared. It was soon realised that the same laws and the same forces operate in organic as in inorganic chemistry. So the terms organic and inorganic have lost their original meaning, and their retention is a matter of convenience. All the so-called organic compounds contain carbon, and since this is the one essential element, **organic chemistry may be defined as the chemistry of the carbon compounds.**

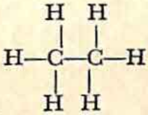
The linking of carbon atoms.—The valency of carbon, almost without exception, is four, and is conveniently represented by four bonds. The carbon atom and the simplest hydrocarbon methane are *graphically* written as follows :



Carbon atom

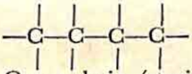


Methane, CH_4

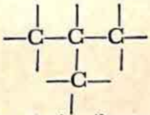


Ethane, C_2H_6

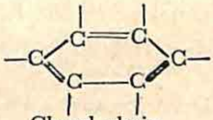
The carbon atom possesses the unique capacity for linking one to another to build up chains of carbon atoms—this property of carbon is known as *catenation*. The chain of carbon atoms may be open (straight or branched) or closed.



Open chain (straight)

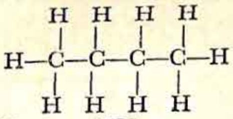


Open chain (branched)

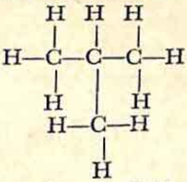


Closed chain

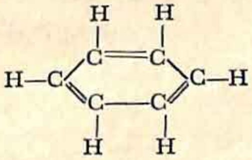
The skeletons of carbon chains such as the above are present in organic compounds. The unused valencies are then satisfied by atoms of hydrogen, oxygen, etc., according to the valency requirements of each carbon atom. When the valencies of the above carbon skeletons are satisfied by hydrogen, we get :



Butane, C_4H_{10}



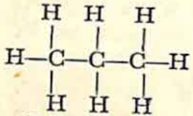
Isobutane, C_4H_{10}



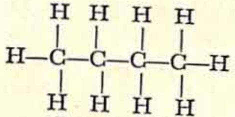
Benzene, C_6H_6

The *theory of carbon linkage*, based on the concept of catenation and quadrivalency of carbon, was developed by the famous German chemist Kekule in 1858. The theory clearly explains the structure of organic compounds.

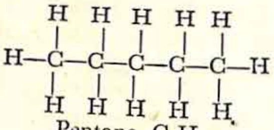
The hydrocarbons.—Carbon forms a large number of compounds with hydrogen, they are known as hydrocarbons. The theory may be further explained with reference to hydrocarbons. Two carbon atoms are linked together in ethane, C_2H_6. Similarly, chains of 3, 4 and 5 carbon atoms are present in propane, butane, and pentane respectively.



Propane, C_3H_8



Butane, C_4H_{10}



Pentane, C_5H_{12}

Methane is a saturated hydrocarbon, since all the valencies of carbon are fully satisfied. When all the valencies of carbon atoms in a chain are fully satisfied, the compound is said to be *saturated*, e.g., ethane, propane, butane. The carbon atoms are linked by *single bonds* in saturated compounds. When the valencies of carbon atoms in a chain are not fully satisfied, the compound is called *unsaturated*. In an unsaturated compound the adjacent carbon atoms may be linked by double bonds, as in ethylene, C_2H_4, and propylene, C_3H_6. The double bond is also called **ethylinic or olefinic linkage.**

$H_2C = CH_2$
Ethylene

$CH_3-CH = CH_2$
Propylene

An unsaturated compound may contain a **triple bond** (also called **acetylinic linkage**) between adjacent carbon atoms, as in acetylene and methyl acetylene.

$H-C\equiv C-H$
Acetylene

$CH_3-C\equiv C-H$
Methyl acetylene

Homologous series.—The number of organic compounds is unbelievably large, but majority of them have been classified into several series of similar structure or constitution and chemical properties. Thus the hydrocarbons of the methane series, e.g., methane, ethane, propane, etc., form such a series, and is collectively known as *paraffins*. The paraffins may be given the general formula C_nH_{2n+2}. The molecular formula of each member of the series differs from that of another which precedes or follow it, by one atom of carbon and two atoms of hydrogen, i.e., by CH_2.

Paraffins, C_nH_{2n+2}			Alcohols, $C_nH_{2n+1}.OH$	
Methane,	CH_4		Methyl alcohol,	CH_3OH
		: difference CH_2		
Ethane	C_2H_6		Ethyl alcohol,	C_2H_5OH
		: difference CH_2		
Propane,	C_3H_8		Propyl alcohol,	C_3H_7OH
		: difference CH_2		
Butane,	C_4C_{10}		Butyl alcohol,	C_4H_9OH
		: difference CH_2		
Pentane, etc., etc.	C_5H_{12}		Amyl alcohol, etc., etc.	$C_5H_{11}OH$

Such a seriest of organic compounds of similar structure (or constitution) and chemical properies, the successive member of which differs in molecular formula by CH_2 only, is called a *homologous series*, and the several members are known as homologues of one another.

Functional groups in organic chemistry.—Berzelius in 1817 recognised that organic compounds are made up of compound radicals—the radicals being linked to one another in the compounds. The structural formula of a given compound readily reveals the radicals present. Ethyl alcohol, $C_2H_5.OH$, for example may be split up into ethyl, C_2H_5-, and hydroxyl, -OH, radicals. Similarly, acetic acid, $CH_3.COOH$, is made up of methyl, $-CH_3$, and carboxyl, -COOH, radicals. Such groups are called *compound radicals* or simply *radicals*.

The (aliphatic) hydrocarbon radicals are derived from corresponding paraffins and have a general formula C_nH_{2n+1}. A hydrocarbon radical, also called *alkyl radical*, contains one hydrogen atom less than a paraffin, and is monovalent, e.g., methyl, CH_3–, ethyl, CH_3-CH_2-, n-propyl, CH_3-CH_2-CH_2-, etc.

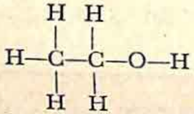
The orderlines that we often come across in organic compounds is by and large due to the characteristic properties that a radical possesses. Hence in the study of organic compounds it is necessary to recognise the existence of principal radicals and know their properties. The consideration of a few homologous series will make things abundantly clear.

Alcohols, $C_nH_{2n+1}.OH$	Amines, $C_nH_{2n+1}.NH_2$
Methyl alcohol $CH_3.OH$	Methyl amine, $CH_3.NH_2$
Ethyl alcohol, $C_2H_5.OH$	Ethylamine, $C_2H_5.NH_2$
Propyl alcohol, $C_3H_7.OH$	Propylamine, $C_3H_7.NH_2$
Butyl alcohol, $C_4H_9.OH$	Butylamine, $C_4H_9.NH_2$
Aldehydes, $C_nH_{2n+1}.CHO$	Acids, $C_nH_{2n+1}.COOH$
Formaldehyde, H.CHO	Formic acid, H.COOH
Acetaldehyde, $CH_3.CHO$	Acetic acid, $CH_3.COOH$
Propionaldehyde, C_2H_5CHO	Propionic acid, $C_2H_5.COOH$
Butyraldehyde, $C_3H_7.CHO$	Butyric acid, $C_3H_7.COOH$

The chemical similarities in members of any particular series is due to some common radical in them, e.g., the properties of aldehydes are due to the presence of the aldehyde radical, $-CHO$; similarly the characteristic properties of alcohols depend on the hydroxyl radical, $-OH$. Such radicals as $-CHO$, $-OH$, $-COOH$, etc., upon which the characteristic properties of different classes of organic compounds largely depend are called **functional groups.** The properties of organic compounds are considered in terms of the radicals they are made up of. Hence it is in the fitness of things that organic compounds have been classified *according to the functional groups they contain*. Some of the principal types of organic compounds are :

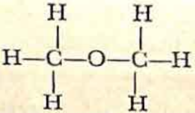
Functional group	Class of compounds	Examples
Hydroxyl, —OH	Alcohols	Ethyl alcohol, $C_2H_5.OH$
Aldehyde, —CHO	Aldehydes	Acetaldehyde, CH_3CHO
Keto, —CO—	Ketones	Acetone, CH_3-CO-CH_3
Carboxyl, —COOH	Acids	Acetic acid, $CH_3.COOH$
Amino, —NH_2	Amines	Methylamine, $CH_3.NH_2$
Amido, —$CONH_2$	Amides	Acetamide, $CH_3.CONH_2$

Isomerism.—The same molecular formula may stand for different organic compounds. Thus the formula C_2H_6O represents both ethyl alcohol and dimethyl ether. When two or more different compounds have the same molecular formula but differ in chemical and physical properties, they are said to be *isomers* of one another, and the phenomenon is known as *isomerism : The isomers differ in structure or constitution*, i.e., in the arrangement of atoms within the molecule. The structural formulae of ethyl alcohol and dimethyl ether will make this clear :



$$\begin{array}{c} \text{H}\ \ \text{H} \\ |\ \ \ | \\ \text{H—C—C—O—H} \\ |\ \ \ | \\ \text{H}\ \ \text{H} \end{array}$$

Ethyl alcohol, CH_3CH_2OH



$$\begin{array}{c} \text{H}\qquad\text{H} \\ |\qquad\ | \\ \text{H—C—O—C—H} \\ |\qquad\ | \\ \text{H}\qquad\text{H} \end{array}$$

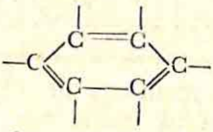
Dimethyl ether, CH_3-O-CH_3

The structural formula attempts to show the manner in which the radicals are combined in an organic compound.

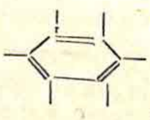
Divisions of organic chemistry.—There are three main divisions : *the aliphatic, the aromatic*, and *the heterocyclic compounds.*

The aliphatic compounds mostly contain *openchain of carbon atoms*, and are, therefore, called *open chain* or *acyclic compounds*. They got their name aliphatic from the fact that natural fats belong to this class. Methane, ethylene, $CH_2 = CH_2$, acetylene, $CH \equiv CH$, ethyl alcohol, CH_3-CH_2OH, acetic acid, $CH_3.COOH$, etc., are aliphatic compounds.

The aromatic compounds are *closed chain* or *carbocyclic compounds*, and contain one or more six-carbon-atom benzene rings. The benzene ring is :

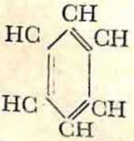


or briefly

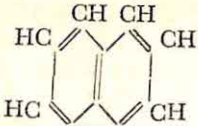


They are all related to the simplest aromatic compound benzene, C_6H_6, and many of them have sweet *aroma* or smell, and hence the name.

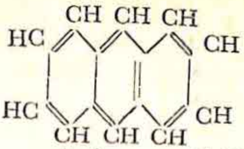
Naphthalene, $C_{10}H_8$, and anthracene, $C_{14}H_{10}$, are aromatic compounds.



Benzene, C_6H_6

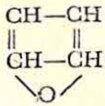


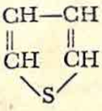
Naphthalene $C_{10}H_8$

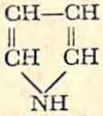


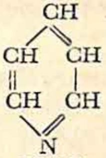
Anthracene, $C_{14}H_{10}$

Heterocyclic compounds are also cyclic compounds, but the rings are not entirely carbocyclic (as in aromatic compounds) but contain atoms of elements besides carbon. e.g.,

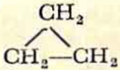

Furan

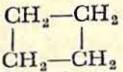

Thiophene

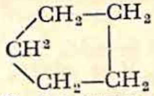

Pyrrole

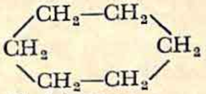

Pyridine

There is a group of carbocyclic or ring compounds which resemble aliphatic compounds in many ways; they are known as *alicyclic* (aliphatic cyclic) compounds. The *naphthenes*, also called *cycloparaffins* or *polymethylenes*, are alicyclic compounds, e.g.


Cyclopropane


Cyclobutane


Cyclopentane


Cyclohexane

Aliphatic Compounds : Paraffins.—The paraffins, also called **alkanes,** are saturated hydrocarbons (i.e. compounds composed of carbon and hydrogen only)—they form a homologous series of the general formula C_nH_{2n+2}. They are characteristically inert and hence the name '*paraffin*' hydrocarbons (Latin, *parum affinis*, little affinity).

Paraffin	B.p.	Paraffin	B.p.
Methane, CH_4	−164°	Pentane, C_5H_{12}	36°
Ethane, C_2H_6	−90°	Hexane, C_6H_{14}	69°
Propane, C_3H_8	−38°	Heptane, C_7H_{16}	98°
Butane, C_4H_{10}	+1°	Octane, C_8H_{18}	125°
		etc., etc.	

The lower paraffins up to and including butane are gases, the members from pentane to pentadecane $C_{15}H_{32}$, are volatile liquids, and the still higher members of the series are solids.

Methane is the first member of the paraffin hydrocarbons. Petroleum or mineral oil is the chief natural source of paraffin hydrocarbons. The crude petroleum is essentially a mixture of gaseous, liquid and solid hydrocarbons, and is the source of petrol, kerosene, paraffin wax, vaseline and the lubricating oil.

Methane or marsh gas, CH_4

Boiling point—161.4° ; m.p.—185.8° ; Solubility, 5.56 volumes in 100 volumes of water at 0° ; 3.3 vols. at 20°C.

Occurrence.—Natural gas from petroleum wells contains more than 90 per cent methane. The *fire damp* of coal mines also contains this gas. Bacterial decay of vegetable matter (cellulose) at the bottom of marshy pools produces methane and hence the name *marsh gas*—the gas escapes in bubbles when the mud is disturbed. Coal gas contains about 35% methane by volume.

Methane may be synthesised : (i) by striking an electric arc between carbon electrodes in an atmosphere of hydrogen : $C + 2H_2 \rightleftharpoons CH_4$,

(ii) by passing a mixture of carbon disulphide vapour and hydrogen sulphide over heated copper : $CS_2+2H_2S+8Cu = CH_4+4Cu_2S$,

(iii) by passing a mixture of carbon monoxide and hydrogen over nickel at about 300°C. $CO + 3H_2 = CH_4 + H_2O$.

Fairly pure methane is evolved by the action of water on aluminium carbide :

$$Al_4C_3 + 12H_2O = 4Al(OH)_3 + 3CH_4.$$

Preparation.—(i) Methane is prepared in the laboratory by strongly heating in a hard glass test tube or copper flask anhydrous sodium acetate with three times its weight of sodalime. The methane is collected over water, in which it is practically insoluble :

$$CH_3COONa + NaOH = CH_4 + Na_2CO_3.$$

The anhydrous sodium acetate is made by heating the crystalline salt in a porcelain basin on a sand-bath until the water is driven off and the salt fuses. It is then cooled in a desiccator, and powdered. The sodalime is a mixture of sodium hydroxide and calcium hydroxide —its use is preferred to caustic soda alone, since it is less fusible than caustic soda, and does not attack glass so readily. The sodalime is made by slaking quick lime with a concentrated solution of caustic soda and drying.

Nearly pure methane is formed by heating sodium acetate with anhydrous barium hydroxide in place of sodalime :

$$2CH_3COONa + Ba(OH)_2 = 2CH_4 + BaCO_3 + Na_2CO_3.$$

Purification.—The gas prepared by this method is not pure and may contain as much as 8% hydrogen and 10% unsaturated hydrocarbons such as ethylene, etc. It is purified by passing in succession through ammoniacal cuprous chloride (to remove acetylene) and conc. H_2SO_4 (to absorb ethylene and moisture), and then collected over mercury. Thus purified methane still contains hydrogen which may be removed as water by mixing the gas with excess oxygen and passing over palladium or platinum black at 100°—the excess oxygen is then removed by alkaline pyrogallol. The methane is finally dried by concentrated sulphuric acid.

(ii) **Pure methane** is prepared by (a) the action of water on zinc methyl, $Zn(CH_3)_2$: $Zn(CH_3)_2 + 2H_2O = Zn(OH)_2 + 2CH_4$.

(b) reducing methyl iodide by means of nascent hydrogen, liberated by the action of zinc-copper couple, (or amalgamated aluminium) on methyl alcohol. CH_3I (methyl iodide) $+ 2H = CH_4 + HI$.

Zinc-copper couple is prepared by immersing granualated zinc in copper sulphate solution until coated with a layer of copper. The couple is washed with water and then with dry methyl alcohol.

The couple is taken in a flask and covered with methyl alcohol (50 c.c.) and a mixture of equal volumes of methyl iodide and methyl alcohol is slowly added from a tap-funnel (fig. 38), when methane is evolved. The gas is passed through a U-tube containing moist Zn-Cu couple to retain the accompanying methyl iodide which is very volatile, and then collected over water. The gas may be dried by conc. H_2SO_4 and collected over mercury. The Zn-Cu couple may act as follows :

$$CH_3I + Zn + CH_3OH = CH_4 + Zn(OCH_3)I.$$

(c) *Grignard reaction.*—Methyl iodide reacts with magnesium in *dry* ether medium, forming methyl magnesium iodide, which is decomposed by adding water, when pure methane is formed.

$$CH_3I + Mg = CH_3MgI$$

$$CH_3MgI + H.OH = CH_4 + Mg(OH)I.$$

Properties.—(i) A colourless gas without smell or taste and about half as light as air, methane is non-poisonous and is slightly soluble in water, but is somewhat more soluble in alcohol. Remerkable for its chemical inertness, the gas withstands the action of acids, alkalis and reducing agents.

Methane is not easily attacked by chemical reagents, and hence the name '*paraffin*' (*parum affinis* : little affinity) for the group of hydrocarbons to which it belongs.

(ii) Non-supporter of combustion, methane burns with a feebly luminous flame, yielding water vapour and carbon dioxide :

$$CH_4+2O_2 = CO_2+2H_2O.$$

(iii) The gas forms an explosive mixture with air or oxygen the ignition of which causes explosion in coal mines.

The use of naked lights in coal mines brings about the ignition of methane and air, resulting in disastrous explosions.

This may be avoided by electric lighting in mines or by the use of *Davy's safety lamp* in which the flame is isolated from the surrounding atmosphere by copper gauze which by its heat conducting capacity prevents the flame from spreading to the surrounding air.

(iv) **Reaction with chlorine.**—Chlorine has no action upon methane in the dark. A mixture of methane and chlorine explodes when ignited or exposed to *bright sunlight*, giving hydrogen chloride and a black cloud of carbon. The reaction shows that methane contains carbon : $CH_4+2Cl_2 = C+4HCl$, but if the mixture is exposed to *diffused sunlight*, chlorine displaces hydrogen from methane, atom by atom,—the ultimate product being carbon tetrachloride. This is a *substitution reaction :*

$CH_4+Cl_2 = HCl+CH_3Cl$ (methyl chloride).
$CH_3Cl+Cl_2 = HCl+CH_2Cl_2$ (methylene chloride).
$CH_2Cl_2+Cl_2 = HCl+CHCl_3$ (chloroform).
$CHCl_3+Cl_2 = HCl+CCl_4$ (carbon tetrachloride).

Methane is a *saturated hydrocarbon*, since all the 4 valencies of carbon are satisfied, and therefore, does not react with hydrogen.

Methane also undergoes substitution with bromine, but with iodine the reaction is reversible. Methane reacts explosively with fluorine.

$$CH_4 + I_2 \rightleftharpoons CH_3I + HI \;; \quad CH_4 + 4F_2 = CF_4 + 4HF$$

Uses of methane : (i) As a source of hydrogen. Methane is mixed with steam and passed over nickel supported on alumina at 725° :

$$CH_4 + H_2O = CO + 3H_2.$$

(ii) For making carbon black—methane is decomposed into carbon and hydrogen at 1000°C : $CH_4 = C + 2H_2$,

(iii) Methane is catalytically oxidised to methyl alcohol CH_3OH and formaldehyde H.CHO.

Unsaturated Hydrocarbons.—The unsaturated hydrocarbons contain less hydrogen atoms than the paraffins with the same number of carbon atoms. There are not, therefore, enough hydrogen atoms in an unsaturated hydrocarbon to satisfy all the valencies of the carbon atoms. These hydrocarbons have the unique property of combining with other elements, e.g., chlorine and bromine, forming *additive compounds*, and are, therefore, called *unsaturated hydrocarbons*. The paraffins do not have this property and are called saturated hydrocarbons. In contrast to the paraffins, the unsaturated hydrocarbons are highly reactive.

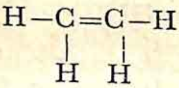
There are two important series of unsaturated hydrocarbons : (i) *the olefines*, and (ii) *the acetylenes*.

Olefines.—*The oleflnes,* also called **alkenes,** form a homologous series of hydrocarbons of the general formula C_nH_{2n} (cf. paraffins C_nH_{2n+2}). They contain *two* hydrogen atoms less than the corresponding paraffin, and possess a *double bond,* also called *oleflnic linkage,* between the two adjacent carbon atoms, e.g., $> C = C <$. The first member of the series ethylene, C_2H_4, contains 2 hydrogen atoms less than required to saturate the valencies of the 2 carbon atoms, and this is true of propylene, C_3H_6, butylene, C_4H_8, and the others.

Olefine (alkene)	Corresponding paraffin (alkane)
Ethylene, C_2H_4 $CH_2 = CH_2$	Ethane, C_2H_6 CH_3-CH_3
Propylene, C_3H_6 $CH_3\text{-}CH = CH_2$	Propane, C_3H_8 $CH_3\text{-}CH_2\text{-}CH_3$

There is no one carbon member olefine corresponding to methane. The name of an olefine is derived from the corresponding paraffin by adding the termination *-ylene* or *-ene* for *-ane*.

Ethylene,



$$H-\underset{H}{\underset{|}{C}}=\underset{H}{\underset{|}{C}}-H$$

Boiling point −103.7 ; m.p. −169.5°. Solubility in water, 0.163 volume in 1 vol. at 18°.

The gas was first discovered by Becher in 1669. It occurs in coal gas to the extent 4—10% by volume.

Preparation.—Ethylene is prepared : (i) by dehydrating ethyl alcohol with concentrated H_2SO_4 or phosphoric acid, or by passing the alcohol vapour over heated alumina. Ethylene or olefiant gas as it is sometimes called, is prepared in the laboratory by 'removing the elements of water' from ethyl alcohol by sulphuric acid. A mixture of about 30 c.c. of ethyl alcohol with 80 c.c. of concentrated sulphuric acid is taken in a flask fitted with a tap-funnel and a delivery tube. The flask (fig. 86) is gently heated to about 160° on a sand bath and a mixture of equal volumes of alcohol and sulphuric acid is slowly added from the tap-funnel as the reaction proceeds. Some glass beads (or a little anhydrous aluminium sulphate)

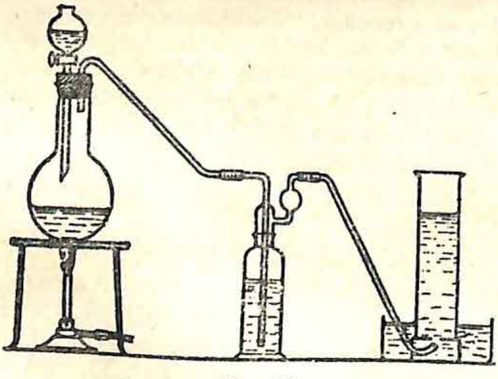


Fig. 86

are placed in the flask to prevent frothing. The reaction takes place in two stages—ethyl hydrogen sulphate first formed decomposes into sulphuric acid and ethylene :

$$C_2H_5OH + H_2SO_4 = C_2H_5HSO_4 + H_2O.$$
$$C_2H_5HSO_4 = C_2H_4 + H_2SO_4.$$

The gas is washed with caustic potash solution to absorb carbon dioxide and sulphur dioxide (formed by the partial reduction of sulphuric acid), and then collected over water. It may be dried by calcium chloride.

Purer ethylene is obtained by dehydrating ethyl alcohol with syrupy phosphoric acid at 230°.

Preparation of ethylene dibromide.—The ethylene gas as made above, is washed with caustic soda solution, and then passed into two wash-bottles containing 10 and 2 c.c.'s of bromine, covered with a layer of water, respectively. The wash-bottles are well-cooled in water. Ethylene is gradually absorbed and bromine becomes paler in colour, and finally a colourless liquid, ethylene dibromide, $C_2H_4Br_2$, is obtained. The liquid is purified by shaking with Na_2CO_3 solution in a separating funnel. The lower, and therefore, the heavier ethylene dibromide layer is then separated, washed with water, and finally dried over calcium chloride and distilled. The distillate between 130-132° is ethylene dibromide.

Pure ethylene is evolved : (i) by heating ethylene dibromide with zinc dust.

$$C_2H_4 + Br_2 = C_2H_4Br_2\ ;\quad C_2H_4Br_2 + Zn = ZnBr_2 + C_2H_4.$$

(ii) by heating ethyl iodide C_2H_5I or ethyl bromide, C_2H_5Br, with an alcoholic solution of caustic potash.

$$C_2H_5I \text{ (ethyl iodide)} + KOH = C_2H_4 + KI + H_2O.$$

Ethylene is technically obtained : (i) by passing ethyl alcohol vapour over heated alumina or kaolin at about 350°C : $C_2H_5OH = C_2H_4 + H_2O$.

(iii) by cracking propane obtained from natural gas.

$$CH_3-CH_2-CH_3 \longrightarrow CH_2 = CH_2 + CH_4$$

Cracked petroleum is an important source of ethylene.

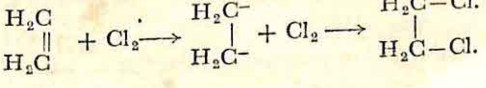
Properties.—(i) Colourless, sweet-smelling gas, ethylene is not poisonous, and has anæsthetic properties. Sparingly soluble in water, the gas is as heavy as air.

(ii) Non-supporter of combustion, the gas burns in air or oxygen —the flame in air is luminous and smoky, and in oxygen bright and smokeless. The gas forms as explosive mixture with air or oxygen :

$$C_2H_4 + 3O_2 = 2CO_2 + 2H_2O.$$

(iii) **Action of chlorine.**—A mixture of ethylene and chlorine burns with a red flame, forming fumes of HCl and clouds of carbon : $C_2H_4 + 2Cl_2 = 2C + 4HCl$,
but when exposed to light at ordinary temperature, an oily liquid, ethylene dichloride, also called **Dutch liquid,** is formed by direct addition : $C_2H_4 + Cl_2 = C_2H_4Cl_2$.

This reaction is typical of many reactions of the *unsaturated hydrocarbon* ethylene (*containing a double bond between the carbon atoms*) in which two monovalent atoms or groups are added to a molecule of ethylene, yielding a saturated additive compound. The reaction with chlorine may be formulated as :



$$\begin{array}{c}H_2C\\ \| \\ H_2C\end{array} + Cl_2 \longrightarrow \begin{array}{c}H_2C-\\ | \\ H_2C-\end{array} + Cl_2 \longrightarrow \begin{array}{c}H_2C-Cl.\\ | \\ H_2C-Cl.\end{array}$$

Ethylene differs from methane in being an *unsaturated hydrocarbon*; it forms compounds by direct addition instead of by substitution, as in the case of methane.

(iv) **Addition reactions.**—An unsaturated hydrocarbon ethylene readily forms addition compounds with :

(a) chlorine, bromine, hydrobromic acid and hydriodic acid.

When ethylene is led into bromine (a red liquid), the latter decolorises forming a colourless liquid ethylene dibromide.

$CH_2 = CH_2 + Br_2 \rightarrow CH_2Br - CH_2Br$ (ethylene dibromide).

$CH_2 = CH_2 + HBr \rightarrow CH_3 - CH_2Br$ (ethyl bromide).

The radical $CH_3 - CH_2 -$ or $C_2H_5 -$ is known as *ethyl*.

(b) hydrogen in presence of reduced nickel catalyst at 150°C :

$$CH_2 = CH_2 + H_2 \rightarrow CH_3 - CH_3 \text{ (ethane).}$$

(c) hypochlorous acid, HOCl :

$CH_2 = CH_2 + HOCl \rightarrow CH_2OH - CH_2Cl$ (ethylene chlorohydrin).

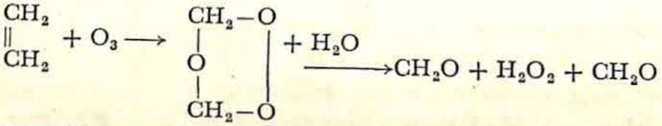
(d) concentrated sulphuric acid slowly in the cold but rapidly at 160°C :

$CH_2 = CH_2 + H.HSO_4 \rightarrow CH_3 - CH_2.HSO_4$ (ethyl hydrogen sulphate)

The ethyl hydrogen sulphate gives ethyl alcohol on boiling with water.

$$CH_3.CH_2.HSO_4 + H.OH = C_2H_5OH + H_2SO_4.$$

(e) Ozone, giving the unstable explosive substance ethylene ozonide which on hydrolysis yields formaldehyde, CH_2O, and hydrogen peroxide. The reaction is useful in detecting double bond in ethylene.



$$\begin{array}{c} CH_2 \\ \| \\ CH_2 \end{array} + O_3 \longrightarrow \begin{array}{c} CH_2-O \\ | \quad\quad | \\ O \quad\quad | \\ | \quad\quad | \\ CH_2-O \end{array} + H_2O \longrightarrow CH_2O + H_2O_2 + CH_2O$$

(v) **Oxidation reactions.**—Mild oxidising agents, such as cold dilute alkaline $KMnO_4$ solution, oxidise ethylene to glycol.

$$CH_2 = CH_2 + H_2O + O \longrightarrow CH_2OH - CH_2OH \text{ (ethylene glycol).}$$

Absorbents.—(i) Bromine ; (ii) Concentrated sulphuric acid—fuming H_2SO_4 rapidly absorbs ethylene.

Test for unsaturation.—The presence of unsaturation in a hydrocarbon is readily detected by its decolorisation of bromine water or of cold dilute alkaline potassium permanganate solution [**Baeyer's test**].

Uses.—(i) In the preparation of mustard gas, and in the artificial ripening of fruits like apples, bananas and oranges, and as an anæsthetic.

(ii) In the preparation of ethylene dibromide for 'ethyl petrol' containing lead tetraethyl ; in the manufacture of ethyl alcohol ; in making the synthetic plastics *polythene* and *teflon*.

The acetylenes.—The **acetylenes,** also called **alkynes** or **alkines,** form a family of unsaturated hydrocarbons of the formula C_nH_{2n-2}. The simplest and the most important member is acetylene, C_2H_2. It contains 2 hydrogen atoms less than ethylene, C_2H_4, and bears the same relation to ethylene, as ethylene does to ethane, C_2H_6.

The acetylenes are named by changing the ending *ane* of paraffins to *yne* or *ine*. Thus :

CH_3-CH_3	$CH_2 = CH_2$	$CH \equiv CH$
Ethane	Ethylene (ethene)	Acetylene (ethine)

The acetylenes contain a *triple bond* between adjacent carbon atoms, and are more unsaturated than the olefines.

Acetylene $CH \equiv CH$

History, *etc.*—Acetylene was discovered by Edmund Davy in 1836 but was carefully studied by Berthelot (1859) who synthesised the gas from its elements by striking an electric arc between two carbon electrodes in an atmosphere of hydrogen (fig. 87). It is highly endothermic.

$$2C + H_2 \rightleftharpoons C_2H_2 - 54{,}860 \text{ cals.}$$

It is found to the extent of 0.6 per cent in coal gas. It is formed when a Bunsen burner 'strikes back'.

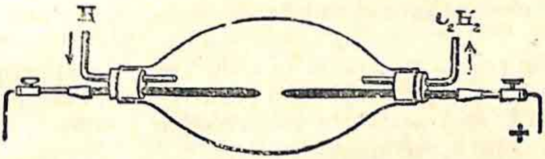


Fig. 87

Laboratory preparation.—Acetylene is prepared in the laboratory, also commercially, by the action of cold water upon calcium carbide.

$$CaC_2 \text{ (calcium carbide)} + 2H_2O = Ca(OH)_2 + C_2H_2.$$

A small heap of calcium carbide is placed on a layer of sand covering the bottom of a conical flask. The air from the flask is first displaced by coal gas, and then water is allowed to drop slowly from a tap-funnel upon the calcium carbide. Acetylene is readily evolved, and is collected over water (fig. 37).

The acetylene from commercial calcium carbide has an unpleasant smell due to presence of hydrogen sulphide and phosphine usually. The crude gas is purified by passing through : (a) acid copper sulphate solution which absorbs the H_2S, and then (b) bleaching powder solution whereby the phosphine is oxidised and retained as phosphoric acid.

Pure acetylene is best obtained : (i) by passing the crude acetylene gas in ammonical cuprous chloride solution which absorbs acetylene, giving a red precipitate of cuprous acetylide, Cu_2C_2, and then decomposing the cuprous acetylide by heating with strong HCl or potassium cyanide solution. The gas may be dried over P_2O_5 and collected over mercury.

$$C_2H_2 + 2CuCl = Cu_2C_2 \text{ (cuprous acetylide)} + 2HCl$$
$$Cu_2C_2 + 2HCl = 2CuCl + C_2H_2$$
$$Cu_2C_2 + 2KCN + 2H_2O = 2CuCN + 2KOH + C_2H_2$$

(iii) by dropping ethylene bromide into boiling alcoholic potash, when pure C_2H_2 evolves. Monobromoethylene or vinyl bromide, $CH_2 = CHBr$, is formed in intermediate stage

$$CH_2Br-CH_2Br + KOH \longrightarrow CH_2 = CHBr + KBr + H_2O$$
$$CH_2 = CHBr + KOH \longrightarrow CH \equiv CH + KBr + H_2O$$

Properties.—(i) A colourless gas with a sweet ethereal smell when pure (the unpleasant smell of the gas is due to the presence of impurities such as phosphine), acetylene is slightly lighter than air, and sparingly soluble in water—the gas is soluble in its own volume of water and *very soluble in acetone.*

(ii) Non-supporter of combustion, the gas burns with a smoky flame, separating much carbon and yielding water and carbon dioxide : $2C_2H_2+5O_2 = 4CO_2+2H_2O$.

A mixture of acetylene and air explodes with violence when ignited. On account of its highly endothermic character, compressed acetylene is likely to detonate, and therefore the gas is stored in solution (under pressure) in acetone absorbed in a porous material—acetone dissolves 300 vols. of the gas under 12 atmospheres.

(iii) **Action of chlorine.**—Acetylene explodes violently if mixed with chlorine, depositing soot : $C_2H_2+Cl_2 = 2C+2HCl$.

When small pieces of calcium carbide are dropped into a saturated solution of chlorine in a jar, there appear flashes of light with simultaneous separation of soot.

But by the regulated action of chlorine on acetylene in presence of a mixture of sulphur chloride and reduced iron, acetylene dichloride, $CHCl = CHCl$, and acetylene tetrachloride (*westron*), $CHCl_2.CHCl_2$ are produced—they are used as solvents.

$$C_2H_2+Cl_2 = C_2H_2Cl_2 \; ; \qquad C_2H_2+2Cl_2 = C_2H_2Cl_4.$$

The acetylene tetrachloride gives trichloroethylene, $CHCl = CCl_2$, (*westrosol*) on heating with lime.

$$2CHCl_2-CHCl_2 + CaO \longrightarrow CHCl = CCl_2 + CaCl_2 + H_2O.$$

This reaction is typical of many reactions of the doubly-unsaturated compound acetylene (containing a triple bond between the carbon atoms) in which 4 univalent atoms or groups are added to a molecule of acetylene to yield an additive compound. The action with chlorine may be represented as :

$$\begin{array}{c}\mathrm{CH}\\ |||\\ \mathrm{CH}\end{array} + Cl_2 = \begin{array}{c}\mathrm{CHCl}\\ ||\\ \mathrm{CHCl}\end{array} \qquad \begin{array}{c}\mathrm{CHCl}\\ ||\\ \mathrm{CHCl}\end{array} + Cl_2 = \begin{array}{c}\mathrm{CHCl_2.}\\ |\\ \mathrm{CHCl_2.}\end{array}$$

(iv) **Addition reactions.**—Acetylene combines additively with :

(a) halogens, halogen hydracids, and strong sulphuric acid, etc.

$$CH \equiv CH+2Br_2 \rightarrow CHBr_2-CHBr_2.$$

$CH \equiv CH+HBr \rightarrow CH_2 = CHBr$ (vinyl bromide).

$CH_2 = CHBr+HBr \rightarrow CH_3-CHBr_2$ (ethylidene bromide).

(b) hydrogen in contact with platinum black or finely divided nickel to form ethylene and then ethane,

$CH \equiv CH+H_2 \rightarrow CH_2 = CH_2$ (ethylene)

$CH_2 = CH_2+H_2 \rightarrow CH_3-CH_3$ (ethane).

Ethylene is made technically by partial hydrogenation of acetylene in presence of palladium at 270°C.

(c) Acetylene is converted by hydration into acetaldehyde by passing into hot dilute sulphuric acid at 60°C, containing mercuric sulphate which acts as a catalyst :

$CH \equiv CH+H_2O \rightarrow CH_3-CHO$ (acetaldehyde).

The acetaldehyde is converted to *ethylalcohol*, CH_3CH_2OH, by reduction by hydrogen in presence of nickel at 100—140°C and to *acetic acid*, CH_3COOH, by oxidation by air in presence of manganous acetate. These reactions are important technically.

$$CH_3-CHO+H_2 = CH_3CH_2OH \; ; \; CH_3-CHO+O = CH_3-COOH$$

(v) **Acetylides.**—Acetylene readily gives a *red precipitate of* cuprous acetylide with ammoniacal cuprous chloride solution and a *white* precipitate of silver acetylide with ammoniacal silver nitrate solution. These reactions provide a **sensitive test** for acetylene.

$$C_2H_2+2CuCl = C_2Cu_2+2HCl \; ; \; C_2H_2+2AgNO_3 = C_2Ag_2+2HNO_3$$

Sodium acetylides C_2HNa and C_2Na_2 are formed by passing acetylene over sodium or a solution of sodium in liquid ammonia. Sodium acetylides are used to prepare alkyl derivatives of acetylene. Thus, sodium acetylide reacts with methyl iodide, CH_3I, in liquid ammonia solution to give methyl acetylene $CH_3.C\equiv CH$.

$$2CH\equiv CH+2Na \longrightarrow 2CH\equiv C.Na+H_2$$

$$CH\equiv CNa+ICH_3 \longrightarrow CH\equiv C.CH_3+NaI.$$

(vi) When *heated to dull redness*, acetylene undergoes polymerisation, yielding benzene : $3C_2H_2 = C_6H_6$.

Acetylene is a highly unsaturated compound and is also very unstable. The greater unstability and higher reactivity of acetylene compared to ethylene (which contains a *double bond*) is due to the presence of a *triple bond* in the molecule.

Absorbents.—Ammoniacal cuprous chloride, bromine, fuming sulphuric acid and acetone are used as absorbents for acetylene.

Uses.—(a) As an illuminant, and for generating oxy-acetylene flame for welding and cutting steel ; (ii) For the manufacture of acetaldehyde, ethyl alcohol and acetic acid ; (iii) In making synthetic rubber and plastics, (iv) Chlorinated acetylene, such as *westron*, $C_2H_2Cl_4$, and *westrosol*, C_2HCl_3, are non-inflammable liquids and are used as solvents for fats, oils and resins.

Comparison of CH_4, C_2H_4 and C_2H_2

Properties	CH_4	C_2H_4	C_2H_2
(i) Nature, colour, smell, etc.	Colourless odourless gas.	Colourless gas with a sweet-smell.	Colourless gas with a sweet smell, if pure.
(ii) Density.	Lighter than air ; density 8 ($H=1$).	Nearly as heavy as air; density 14 ($H = 1$).	Slightly lighter than air ; density 13 ($H = 1$)
(iii) Solubility in water.	Sparingly soluble ; 5.56 vols. in 100 vols. at 0°C ; 3.3 vols. at 20°C.	Slightly soluble ; 0.163 vol. in 1 vol. at 13°C.	1 vol. in 1 vol. at 15° ; *Very soluble in acetone.*
(iv) Combustibility, etc.	Non-supporter of combustion ; burns with a feebly luminous flame.	Non-supporter of combustion ; burns with a luminous flame.	Non-supporter of combustion ; burns with a sooty flame.
(v) When mixed with air or O_2 and fired.	Explodes violently ; 1 vol. requires 2 vols. of O_2.	Explodes violently ; 1 vol. requires 3 vols. of O_2.	Detonates explosively ; 1 vol. requires 2.5 vols. of O_2.

Properties	CH_4	C_2H_4	C_2H_2
(vi) Action of H_2.	No action, since CH_4 is a *saturated hydrocarbon*.	An *unsaturated* hydrocarbon with a *double bond* reacts additively with 2 atoms of H_2 in presence of Ni-catalyst : $C_2H_4+H_2=C_2H_6$	An *unsaturated* hydrocarbon with a *triple bond* reacts additively with 4 atoms of H_2 in presence of Ni-catalyst : $C_2H_2+2H_2=C_2H_6$
(vii) Action of chlorine.	(i) Explodes in direct sunlight, forming HCl and C. $CH_4+2Cl_2 = C+4HCl$. (ii) Forms substitution products CH_3Cl, CH_2Cl_2, $CHCl_3$ and CCl_4 in diffused sunlight, since CH_4 is a saturated hydrocarbon.	(i) Burns when ignited, forming HCl and C. $C_2H_4+2Cl_2=2C+4HCl$. (ii) Reacts additively with 2 toms of Cl_2. a$C_2H_4+Cl_2=C_2H_4Cl_2$, since C_2H_4 is unsaturated and contains a double bond.	(i) Bursts into flame, forming HCl and C. $C_2H_2+Cl_2=2C+2HCl$. (ii) Reacts additively with 4 atoms of Cl_2 in presence of sulpher chloride : $C_2H_2+2Cl_2=C_2H_2Cl_4$. since C_2H_2 is unsaturated and contains a triple bond.
(viii) Action of halogen acids, HBr HI, etc.	No action.	Adds 1 molecule, $C_2H_4+HBr=C_2H_5Br$.	Adds 2 molecules. $C_2H_2+2HBr=C_2H_4Br_2$.
(ix) Bromine water or cold dilute alkaline $KMnO_4$.	No action	Decolorises, hence unsaturated.	Decoloursises, hence unsaturated .
(x) Ammoniacal Cu_2Cl_2 solution.	No action.	No action.	Red precipitate of Cu_2C_2.
(xi) Absorbent.	—	Bromine and fuming H_2SO_4.	Bromine and fuming H_2SO_4 ; also ammonical Cu_2Cl_2 solution.

Separation of CH_4, C_2H_4 and C_2H_2

The gas mixture is passed through ammonical cuprous chloride solution when C_2H_2 alone is absorbed, forming red precipitate of Cu_2C_2.

Red precipitate of Cu_2C_2 is boiled with KCN solution—pure C_2H_2 is given off.

The mixture of residual gases CH_4 and C_2H_4 is passed through fuming H_2SO_4, when C_2H_4 alone is absorbed forming ethyl hydrogen sulphate.

The liquid containing ethyl hydrogen sulphate gives off C_2H_4 on heating.

The unabsorbed gas is CH_4.

Chloroform, trichloromethane, $CHCl_3$, is formed when chlorine acts on methane in sunlight It is prepared in the laboratory and also commercially by boiling ethyl alcohol or acetone with bleaching powder and water. The bleaching powder supplies both chlorine and lime for the reaction.

(i) Alcohol is first oxidised by chlorine to aceteldehyde, CH_3CHO. The acetaldehyde reacts with more chlorine, giving trichloroacetaldehyde or chloral, $CCl_3.CHO$. The chloral is decomposed by lime into chloroform and calcium formate.

$$CH_3CH_2OH \text{ (ethyl alcohol)} + Cl_2 = CH_3CHO + 2HCl$$

$$CH_3CHO \text{ (acetaldehyde) } + 3Cl_2 = CCl_3CHO + 3HCl$$

$$2CCl_3CHO + Ca(OH)_2 = 2CHCl_3 + (HCOO)_2Ca.$$

(ii) Acetone reacts with chlorine, giving trichloro acetone, which is decomposed by lime, giving chloroform and calcium acetate.

$$CH_3CO.CH_3 \text{ (acetone)} + 3Cl_2 = CCl_3.CO.CH_3 + 3HCl$$

$$2CCl_3.CO.CH_3 + Ca(OH)_2 = 2CHCl_3 + (CH_3COO)_2Ca$$

Preparation.—Fresh bleaching powder (200 gm.) is ground into a paste with water (800 c.c.) and then placed in a two-litre flask fitted with a condenser and receiver (fig. 88) 50 c.c. acetone, diluted with 50 c.c. water, are then added in small amounts. The flask is then heated on a water bath for about half an hour. Chloroform distils with some acetone and water, and collects as a heavy oil in the receiver. Distillation is continued until no more oily drops pass over. It is purified by shaking several times with *sodium carbonate* solution (to remove the acid) in a separating funnel—two layers separate on keeping, the lower layer of chloroform is run out. It is then similarly washed with water (to remove excess of sodium carbonate) in the separating funnel and finally dried over *fused calcium chloride* and redistilled. The distillate between 58 to 62° is collected.

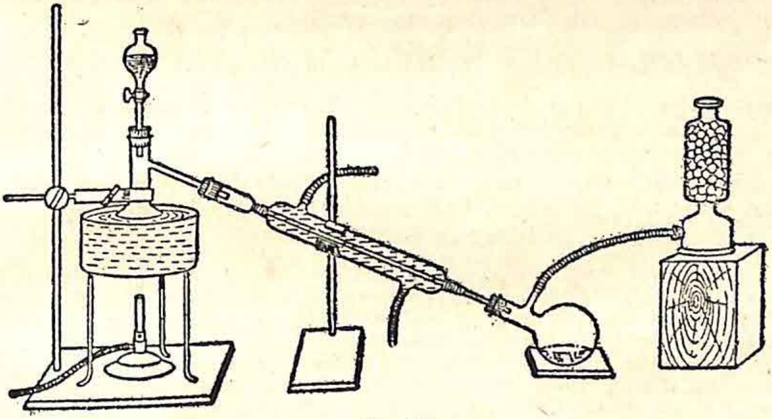


Fig. 88

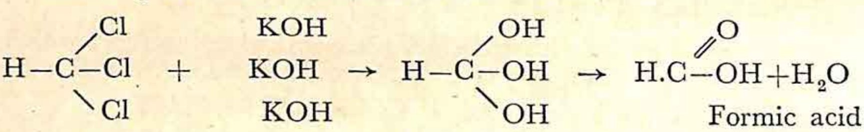
Chloroform is also made commercially by reducing carbon tetrachloride, CCl_4, with iron and water : $CCl_4+2H = CHCl_3+HCl$.

Pure chloroform is made by heating chloral with aqueous caustic soda. $NaOH+CCl_3.CHO$ (chloral) $= CHCl_3+HCOONa$.

Properties.—(i) Chloroform is a heavy (sp. gr. 1.5 at 15°) colourless liquid (b.p. 61°) with a pleasant smell. It is non-inflammable. It is insoluble in water, but readily dissolves in alcohol and ether.

(ii) On hydrolysis with hot alcoholic potash, it gives potassium formate $CH.Cl_3+4KOH = H.COOK+3KCl+2H_2O$.

The stages in the reaction are as follows :—



$$\mathrm{H{-}C(Cl)_3 + 3\,KOH \rightarrow H{-}C(OH)_3 \rightarrow H.C({=}O){-}OH+H_2O}$$

Orthoformic acid

The intermediate compound, orthoformic acid, is unstable, and readily splits off water, forming formic acid.

(iii) When chloroform is warmed with few drops of aniline, $C_6H_5NH_2$, and alcoholic potash, an extremely nauseating smell is produced, owing to the formation of highly poisonous *phenyl carbylamine* or *phenyl isocyanide*, C_6H_5NC. This forms a delicate *test* for chloroform and is known as the carbylamine reaction.

$$C_6H_5NH_2+CHCl_3+3KOH = C_6H_5NC+3KCl+3H_2O$$

Uses.—Chloroform is used, usually mixed with ether, in surgery as an anæsthetic —its vapour produces unconsciousness on inhalation. But chloroform for anæsthetic purpose must be strictly pure.

In presence of sunlight and air, chloroform slowly decomposes into HCl and carbonyl chloride (or phosgene), $COCl_2$, which is highly poisonous.

$$2CHCl_3+O_2 = 2COCl_2+2HCl$$

The presence of products of decomposition may be ascertained by adding silver nitrate solution which forms a white precipitate of silver chloride, if $COCl_2$ or HCl is present. Pure chloroform gives no precipitate with silver nitrate solution. Chloroform for anæsthetic purposes should be kept in well-stoppered bottles of dark blue or brown glass, full to the neck, with addition of about one per cent alcohol (which arrests the decomposition of chloroform). Even then it is desirable to keep the bottles in the dark. Chloroform is an excellent solvent for many organic substances; it dissolves fats, oils, rubber, etc. Chloroform combines with acetone to give *chloretone*, which is a hypnotic.

XXV

ALCOHOLS

Alcohols.—The alcohols may be looked as paraffins in which one or more hydrogen atoms are replaced by hydroxyl groups, OH. The alcohols are, therefore, hydroxyl derivatives of paraffins. According to the number of OH groups present in the compound, they are called *mono-*, *di-*, *tri-*, etc., *hydric* alcohols. Alcohols containing more than one OH group, are in general, known as polyhydric alcohols.

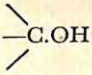
Paraffin	*Name of alcohol*	*Class*
Methane, CH_4	Methyl alcohol, CH_3OH	Monohydric alcohol
Ethane, C_2H_6	Ethyl alcohol, CH_3CH_2OH	,, ,,
	Glycol, $CH_2OH.CH_2OH$	Dihydric ,,
Propane, C_3H_8	Glycerol, $CH_2OH.CHOH.CH_2OH$	Trihydric ,,

Monohydric alcohols.—They are mono-hydroxy derivatives of paraffins. They contain an alkyl group attached to a hydroxyl and have the general formula $C_nH_{2n+1}OH$.

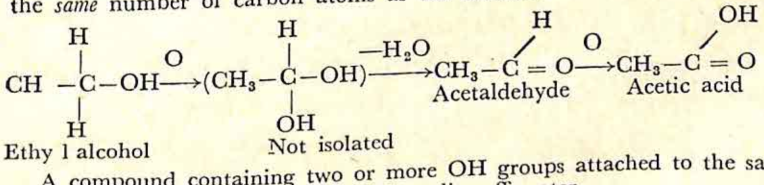
They are named from the corresponding paraffin by replacing the suffix -'*ane*' by -'*yl*' (or by deleting final '*e*' and adding the ending '*ol*').

Methane, CH_4	Methyl alcohol, methanol, CH_3OH
Ethane, C_2H_6	Ethyl alcohol, ethanol, C_2H_5OH
Propane, C_3H_8	Propyl alcohol, propanol, C_3H_7OH

An alcohol is known as **primary, secondary,** or **tertiary,** according as it contains a $-CH_2OH$, $= CHOH$, or a $\equiv C.OH$ group in the molecule

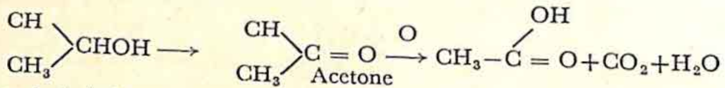
Typye of alcohol	*Typical group*	*Example*
Primary alcohol	$-CH_2OH$	Methyl alcohol, $H.CH_2OH$ Ethyl alcohol, $CH_3.CH_2OH$ Normal propyl alcohol $CH_3.CH_2.CH_2OH$
Secondary alcohol	$> CHOH$	Isopropyl alcohol or secondary propyl alcohol, $CH_3-CHOH-CH_3$
Tertiary alsohol	 C.OH	Tertiary butyl alcohol, $CH_3-\underset{\substack{\vert \\ CH_3}}{C}(OH)-CH_3$

A **primary alcohol** on oxidation first gives an *aldehyde*, and then an *acid* containing the *same* number of carbon atoms as the alcohol.



A compound containing two or more OH groups attached to the same carbon atom, is usually unstable and readily splits off water.

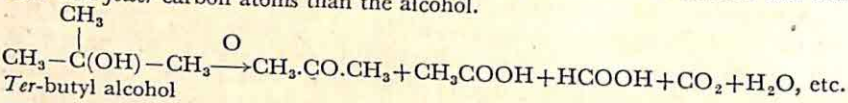
A **secondary alcohol** on oxidation gives a *ketone* with the *same* numbers of carbon atoms as the alcohol, and then acids with *fewer* carbon atoms, on further oxidation.



$$\begin{matrix}CH\\CH_3\end{matrix}\!\!>CHOH \longrightarrow \begin{matrix}CH\\CH_3\end{matrix}\!\!>\underset{Acetone}{C=O} \xrightarrow{O} CH_3-\overset{OH}{C}=O+CO_2+H_2O$$

Sec—propyl alcohol

A **tertiary alcohol** on drastic oxidation gives a mixture of ketones and acids, each with *fewer* carbon atoms than the alcohol.



$$CH_3-\overset{\overset{CH_3}{|}}{C}(OH)-CH_3 \xrightarrow{O} CH_3.CO.CH_3+CH_3COOH+HCOOH+CO_2+H_2O, \text{ etc.}$$

Ter-butyl alcohol

The three types of alcohols may be *distinguished* in this way.

Methyl alcohol, methanol.—One of the products of dry distillation of wood is the aqueous distillate *pyroligneous acid* (p.180), which consists mainly of about 1% methyl alcohol, 5-8% acetic acid and 0.1% acetone. The pyroligneous acid is first neutralised with milk of lime, whereby acetic acid is converted into calcium acetate and then distilled—the methyl alcohol together with acetone and water passes into the distillate and calcium acetate is left behind as a residue. The methyl alcohol (b.p. 65°) is then separated from most of the acetone (b.p. 56°) by careful fractional distillation. The mehyl alcohol may be *dried* by standing over quick lime, followed by re-distillation. The last trace of water may be removed by distillation over metallic calcium. But the methyl alcohol thus prepared invariably contains about 1—2 per cent acetone.

Methyl alcohol is also called *wood spirit* or *wood naphtha*, as it is made by distillation of wood. Methyl alcohol is a colourless liquid (b.p. 64.7°), miscible with water and ether. It is inflammable and is poisonous and hence its use to *denature* ethyl alcohol (*i.e.*, to make it unfit to drink) in making methylated spirit.

Uses of methyl alcohol.—Methyl alcohol is used : (i) in making methylated spirit, and in the preparation of formaldehyde, various dye intermediates and perfumes, (ii) as a solvent for shellacs and resins in the preparation of varnishes, (iii) as an anti-freeze in radiators of motor cars, and (iv) as a motor fuel mixed with petrol.

Ethyl alcohol, ethanol, C_2H_5OH, is simply called 'alcohol', also known as *grain alcohol* or *spirit of wine* in commerce. It is usually made by *fermentation* of certain sugars, such as glucose and cane sugar, by yeast. Thus, when yeast is added to a solution of glucose at the room temperature, the liquid shortly begins to froth, giving the appearance of boiling. The process is known as *fermentation* from the Latin *fervere*, to boil. The glucose is decomposed into ethyl alcohol and carbon dioxide during fermentation :

$$C_6H_{12}O_6 \text{ (glucose)} = 2C_2H_5OH + 2CO_2$$

The decomposition is effected by certain substance, called **enzymes,** which are produced by yeast during its growth.

The enzymes are complex organic substances with act as catalysts. Yeast is a low form of plant life consisting of one cell only.

Fermentation is, therefore, a process of decomposition of complex organic substances into simpler ones, brought about by enzymes (produced by yeast, etc.) which act as catalysts in the process.

The *ferment* or the *enzyme*, called *zymase*, present in yeast cells, converts glucose into alcohol and carbon dioxide. The change of glucose (or fructose) into ethyl alcohol is known as **alcoholic fermentation.**

Although a living organism yeast is used in the alcoholic fermentation, the process is *merely a chemical reaction*, since the zymase extracted by a process in which the yeast cells are destroyed, sets in fermentation like the living yeast.

The yeast contains several enzymes ; among which are *zymase*, *invertase* and *maltase*. Invertase catalyses the decomposition of cane sugar by hydrolysis into glucose, $C_6H_{12}O_6$, and fructose, $C_6H_{12}O_6$.

$$C_{12}H_{22}O_{11} \text{ (cane sugar)} + H_2O = C_6H_{12}O_6 + C_6H_{12}O_6$$

Maltase converts maltose (a sugar isomeric with cane sugar) into two molecules of glucose.

$$C_{12}H_{22}O_{11} \text{ (maltose)} + H_2O = 2C_6H_{12}O_6 \text{ (glucose)}$$

Invertase and maltase are thus hydrolytic enzymes. Zymase, as already stated, brings about alcoholic fermentation.

Manufacture.—Ethyl alcohol is made from cheap raw materials : (i) molasses, (ii) starchy materials such as rice, maize, potato, etc.

(i) Molasses is the mother liquor left after crystallisation of cane-sugar from the concentrated cane juice. It contains about 50-60 per cent cane sugar. It is available from sugar mills and is an important source of alcohol in India and elsewhere.

The molasses is diluted with water to about 10-15 per cent sugar, and is fermented by adding yeast in slightly acid medium. The yeast has a double function upon the cane sugar—the enzyme *invertase* converts it into glucose and fructose, which are then fermented into ethyl alcohol under the influence of *zymase*, as already stated. The fermented liquor contains 6—12% alcohol. The process takes about 2 days.

(iii) The starch-containing materials, such as rice and potato, are reduced to a pulp or a paste with water, and then mixed with a little *malt*. Starch is not directly fermentable by yeast, and must, therefore, be first converted into sugar. The enzyme *diastase* present in germinating barley ('malt') converts starch into the sugar, *maltose*, $C_{12}H_{22}O_{11}$. The mixture is kept at about 50° for about 30-60 minutes, when maltose is formed.

$$2(C_6H_{10}O_5)_n \text{ (starch)} + nH_2O = nC_{12}H_{22}O_{11} \text{ (maltose)}.$$

The liquid is then cooled to about 25° and mixed with yeast. The mixture is kept for 2-3 days, when the maltose is first converted into glucose, which then undergoes alcoholic fermentation, in a manner as stated above.

The weak solution of alcohol (6-12%) is then submitted to fractional distillation in large stills (e.g., Coffey's still) using a fractionating column, whereby a distillate containing about 95.6% alcohol is obtained and is commercially known as **rectified spirit.** But absolute alcohol, free from water, cannot be made by the above method as a constant boiling mixture of 95.6% alcohol and 4.4% water, boiling at 78.15°, distils over. The **absolute alcohol** is made in two ways :

(i) The rectified spirit is dried by standing over quick lime, and then distilled. But it still contains traces of water which may be removed by adding calculated amount of Na or Ca, and then re-distilling.

(ii) The rectified spirit is mixed with a little benzene and distilled. Distillation yields first (a) a mixture of benzene, alcohol and water (b.p. 64.8), then (b) a mixture of benzene and alcohol, (b.p. 68.2) and finally (c) a distillate of pure anhydrous alcohol (b.p. 78.5).

The anhydrous alcohol is known as *absolute alcohol*.

Synthetic ethyl alcohol is made from ethylene (which is obtained from cracked petroleum). Ethylene is absorbed in concentrated sulphuric acid, and the resulting ethyl hydrogen sulphate, $C_2H_5HSO_4$, when heated with dilute sulphuric acid, undergoes hydrolysis, giving ethyl alcohol.

$$CH_2 = CH_2 + H_2SO_4 = CH_3-CH_2.HSO_4$$

$$CH_3-CH_2.HSO_4 + H.OH = CH_3\text{-}CH_2OH + H_2SO_4$$

Properties.—Pure ethyl alcohol is a colourless liquid (b.p. 78.5° ; sp. gr. 0.790 at 15°) with a pleasant vinous smell and a burning taste. It is inflammable and burns with a pale blue flame. It is miscible with water with evolution of heat and contraction in volume. The alcohol itself is very hygroscopic. It is also miscible with ether. It freezes at—114° and hence its use in alcohol thermometers. Bromine, iodine, sulphur, and phosphorus, all dissolve in ethyl alcohol. In small doses the alcohol is a good stimulant, but in larger doses causes blurring of senses and finally unconsciousness.

Quick lime is a suitable drying agent for alcohol. Calcium chloride *cannot* be used, as it combines with the alcohol, yielding a compound, $CaCl_24C_2H_5OH$, containing alcohol of crystallisation.

Reactions.—The imporatnt reactions of ethyl alcohol (a typical monohydric alcohol)are :

(i) Metallic sodium (or potassium) vigorously reacts with alcohol, evolving hydrogen and forming *ethoxide* or *ethylate* (white crystalline deliquescent solid).

$$2C_2H_5OH + 2Na = 2C_2H_5ONa \text{ (sodium ethoxide)} + H_2$$

Metallic Ca, Mg, etc., also react similarly but less rapidly. The reaction is used to remove traces of water from alcohol.

The ethoxides are radily hydrolysed by water, giving back alcohol.

$$C_2H_5ONa + H.OH = C_2H_5OH + NaOH$$

(ii) PCl_5 reacts, forming ethyl chloride, $POCl_3$ and HCl.

$$C_2H_5OH + PCl_5 = C_2H_5Cl + POCl_3 + HCl$$

Reactions (i) and (ii) detect OH group in alcohols.

(iii) It reacts with acids in presence of a dehydrating agent, such as concentrated H_2SO_4, HCl gas, etc., forming an *ester* and water. Alcohol + acid $\leftrightharpoons$ ester + water.

The process of esterification is reversible. The dehydrating agent absorbs the water formed, and thereby the reaction may be made complete.

(a) Acetic acid acts on ethyl alcohol in presence of conc. H_2SO_4, giving the ester, ethyl acetate, $CH_3COOC_2H_5$, which has a fruity smell.

$$CH_3COOH+HOC_2H_5 \leftrightharpoons CH_3COOC_2H_5+H_2O$$

(b) HCl gas reacts in presence of anhydrous zinc chloride, giving ethyl chloride. HBr and HI act similarly.

$$C_2H_5OH+HCl \leftrightharpoons C_2H_5Cl+H_2O$$

(c) Concentrated H_2SO_4 reacts with ethyl alcohol, giving ethyl hydrogen sulphate. $C_2H_5OH+H_2SO_4 \leftrightharpoons C_2H_5HSO_4+H_2O$.

The ethyl hydrogen sulphate, on hydrolysis with hot dilute H_2SO_4, gives back the alcohol.

At about 140° ethyl hydrogen sulphate reacts with more alcohol giving diethyl ether, $C_2H_5-O-C_2H_5$.

$$C_2H_5HSO_4+HOC_2H_5 = C_2H_5-O-C_2H_5+H_2SO_4$$

At a still higher temperature, about 180°, ethyl hydrogen sulphate gives ethylene. $C_2H_5HSO_4 \leftrightharpoons CH_2 = CH_2+H_2SO_4$.

(iv) Oxidising agents, e.g., $K_2Cr_2O_7$ and conc. H_2SO_4, convert the alcohol first into acetaldehyde, CH_3CHO, and finally into acetic acid.

$$CH_3CH_2OH+O = CH_3CHO+H_2O \; ; \; CH_3CHO+O = CH_3COOH$$

Dehydrogenation by passing the alcohol vapour over heated copper at 300°, also forms acetaldehyde. $CH_3CH_2OH = CH_3CHO + H_2$.

(v) Dehydration of alcohol by passing over alumina at 350° gives ethylene. Concentrated H_2SO_4 also dehydrates ethyl alcohol :

$$C_2H_5OH \rightarrow CH_2 = CH_2+H_2O.$$

(iv) Red P and bromine (or iodine) act on alcohol, giving ethyl bromide (or iodide). $PBr_3+3C_2H_5OH = 3C_2H_5Br+H_3PO_3$.

(vii) Chlorine acts on ethyl alcohol, first giving acetaldehyde, and finally trichloro-acetaldehyde or chloral, CCl_3CHO. Bromine racts similarly, giving bromal, $CBr_3.CHO$, but iodine has no action.

$$CH_3CH_2OH + Cl_2 = CH_3CHO+2HCl$$
$$CH_3CHO+3Cl_2 = CCl_3.CHO+3HCl$$

(viii) Action of bleaching powder and water gives chloroform.

(ix) Iodine reacts in presence of aqueous alkali, giving iodoform.

Presence of traces of water in alcohol may be detected by adding anhydrous copper sulphate which turns blue, or by adding few drops of benzene or petroleum ether which gets turbid, if any water is present :

Tests for ethyl alcohol.—Use an aqueous solution of ethyl alcohol.

Reagent	Ethyl alcohol
(i) Iodine + NaOH warm*	Yellow crystals of iodoform
(ii) $K_2Cr_2O_7+H_2SO_4$ (1 : 1) Distil	Distillate is acetaldehyde
(iii) Acetic acid + H_2SO_4 Warm	Fruity smell of ethyl acetate
(iv) Plunge red-hot Cu-gauge into the solution**	Acetaldehyde is formed

* A few crystals of iodine (or a solution of iodine in potassium iodide) is added to the aqueous solution of alcohol. The mixture is warmed and caustic soda solution is added, drop or drop, until the colour of iodine disappears. Yellow crystals of iodoform with characteristic smell are deposited on cooling.

** Acetaldehyde gives a violet colour with Schiff's reagent at ordinary temperature.

Uses of ethyl alcohol.—The uses of alcohol is very extensive. It is used : (i) in making iodoform, chloroform, ether, acetaldehyde, vinegar, and transparent soaps, (ii) in the preparation of dyes, drugs, perfumes (ethyl esters make fruit essences and perfumes), synthetic rubber, and rayon, (iii) in the preparations of **tinctures** (alcoholic solutions of extracts of medicinal substances), e.g., tincture of iodine, and tonic, (iv) as alcoholic beverages, e.g., wine, beer, etc., (v) as a solvent for gums and resins in making lacquers and varnishes, (vi) as a preservative of biological specimens and for sterilisation in surgery, (vii) as an anti-freeze in radiators, (ix) as a fuel in internal combustion engines. Mixed with petrol, it is used in automobiles. The alcohol thus used in getting power is often called *power alcohol*, and (x) in making methylated spirit.

Methylated spirit.—All the alcoholic beverages are subject to high excise duty. But 'denatured' alcohol, unfit for drinking purposes but suitable for general scientific and industrial work, is duty-free, and therefore, cheap. The denatured alcohol is known as methylated spirit, and consists of about 90% rectified spirit, 10% wood spirit, and a little pyridine. The methyl alcohol (wood spirit) and pyridine render the alcohol poisonous and unpalatable and consequently unfit to drink. The methylated spirit is used in making dyestuffs, varnishes and fine chemicals. It is used in spirit lamps.

Solidified spirit is made by dissolving soap in rectified spirit, and then cooling the solution, when it gets to a solid mass. It is easily ignited and is used in lamps. Approximate percentage of alcohol in several alcoholic beverages are :

Beer 2-5 ; wine 7-11 ; claret 7 ; sherry 16 ; port 20 ; whisky, brandy, rum 35-40.

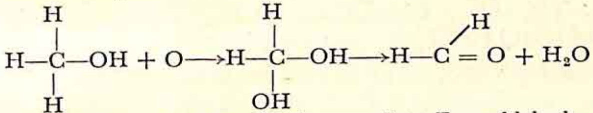
The percentage of alcohol in pharmaceutical preparations is high : tincture of iodine 80-85 ; spirit of ammonia 62-68 ; spirit of camphor 80-87.

The percentage of alcohol in a sample of aqueous spirit, e.g., rectified spirit, is readily determined by measuring the specific gravity with a hydrometer and then referring to standard tables in which sp. gr. of any mixture of alcohol and water is given.

XXVI

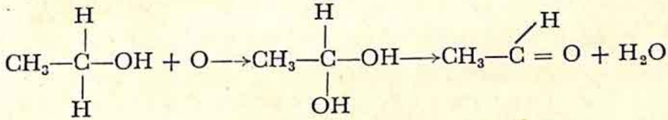
ALDEHYDES AND KETONES

Aldehydes and ketones.—A primary alcohol on mild oxidation yields an *aldehyde*, which contain two hydrogen atoms less than the alcohol and hence the name aldehyde from *alcohol dehydrogenation*. On cautious oxidation methyl alcohol gives formaldehyde, and ethyl alcohol acetaldehyde :



$$\mathrm{H{-}\underset{H}{\overset{H}{C}}{-}OH} + \mathrm{O} \longrightarrow \mathrm{H{-}\underset{OH}{\overset{H}{C}}{-}OH} \longrightarrow \mathrm{H{-}\overset{H}{C}{=}O} + \mathrm{H_2O}$$

Methyl alcohol Unstable intermediate Formaldehyde



$$\mathrm{CH_3{-}\underset{H}{\overset{H}{C}}{-}OH} + \mathrm{O} \longrightarrow \mathrm{CH_3{-}\underset{OH}{\overset{H}{C}}{-}OH} \longrightarrow \mathrm{CH_3{-}\overset{H}{C}{=}O} + \mathrm{H_2O}$$

Ethyl alcohol Unstable intermediate Acetaldehyde

The unstable intermediates having two OH groups linked to the same carbon atom readily eliminate water.

All aldehydes contain the aldehydic group $\mathrm{{-}\overset{H}{C}{=}O}$, and the type formula for aldehydes is $\mathrm{R{-}\overset{H}{C}{=}O}$, where R is an alkyl group, except for the first member of the series, formaldehyde which is $\mathrm{H{-}\overset{H}{C}{=}O}$. All ketones contain the ketone group $>\mathrm{C}=\mathrm{O}$, and the type formula for ketones is $\begin{matrix}\mathrm{R}\\ \mathrm{R'}\end{matrix}\!\!>\mathrm{C}=\mathrm{O}$, where R and R′ are identical or different alkyl groups :

$CH_3\text{-}CO\text{-}CH_3$	$CH_3\text{-}CO\text{-}C_2H_5$
Dimethyl ketone	Methyl ethyl ketone

The aldehyde and ketone, therefore, both contain the group $>\mathrm{C}=\mathrm{O}$; thin is known as the *carbonyl group*, and this accounts for many similar reactions of aldehydes and ketones.

Acetaldehyde, CH_3CHO, is made : (i) by oxidising ethyl-alcohol with sodium or potassium dichromate and concentrated sulphuric acid, in the laboratory.

$$CH_3CH_2OH + O = CH_3CHO + H_2O.$$

Preparation.—Coarsely powdered sodium dichromate (100 g.) and water (400 c.c.) are placed in a two litre flask fitted with a tap funnel, and attached to a condenser and receiver. Ice-cold water circulates through the condenser and the receiver is cooled in ice. A mixture of absolute alcohol (125 c.c.) and concentrated sulphuric acid (75 c.c.) is slowly run into the flask. The flask is heated on a water bath, and the distillate which contains acetaldehyde and some alcohol and water, collects in the receiver.

The distillate is then taken in a flask fitted with a fractionating column and *gently* warmed from a water bath, when acetaldenyde (b.p. 21°) passes over (leaving alcohol and water behind) and is led into dry ether taken in a wash bottle, coold in ice.

The ethereal solution is then saturated with *dry* ammonia gas, when crystals of acetaldehyde-ammonia deposit. The crystals are separated and decomposed by distilling with dilute sulphuric acid. The distilate of acetaldehyde is dried over calcium chloride and re-distilled. Pure acetaldehyde is collected in a ice-cold receiver.

$$CH_3CHO + NH_3 = CH_3\text{-}CH(OH).NH_2$$

$$CH_3CH(OH).NH_2 + H_2SO_4 = CH_3CHO + NH_4HSO_4$$

(ii) by distilling a dry mixture of calcium acetate and calcium formate.

$$\begin{array}{l} CH_3-CO-OCaO-CO-CH_3 = 2CH_3HCO + 2CaCO_3 \\ HCO.OCaO.CO.H \end{array}$$

(iii) by passing vapours of acetic acid and formic acid over a catalyst of manganous oxide, MnO, at 300°.

$$CH_3COOH + HCOOH = CH_3CHO + H_2O + CO_2$$

(iv) by passing a mixture of alcohol vapour and air over copper or silver catalyst at dull red heat.

$$CH_3CH_2OH + O = CH_3CHO + H_2O.$$

(v) by reduction of acetyl chloride by hydrogen in presence of palladium at 150°. $CH_3COCl + H_2 = CH_3CHO + HCl.$
All the above processes illustrate general methods for the preparation of aldehydes.

(vi) by hydration of acetylene by passing into 20 per cent sulphuric acid containing mercuric sulphate as a catalyst, and kept at about 80°. Acetaldehyde is separated by fractional distillation.

$$CH \equiv CH + H_2O = CH_3CHO$$

Methods (iv) and (vi) are used for commercial preparation of acetaldehyde.

Properties.—Acetaldehyde is a colourless gas (b.p. 21°) with a suffocating smell. It is soluble in water, alcohol and ether.

General properties of acetaldehyde and acetone.—The chemical properties of acetaldehyde, CH_3CHO, and acetone, $CH_3\text{-}CO\text{-}CH_3$, are similar in many respects, and this is due to the presence of carbonyl group, $>C=O$, in both.

(i) **Oxidation :** Aldehydes readily undego oxidation (with dichromate and sulphuric acid), giving acid with *same* number of carbon atoms. Acetaldehyde gives acetic acid.

$$CH_3CHO + O = CH_3COOH \text{ (acetic acid)}$$

Ketone, e.g., acetone, is far less readily oxidised. On drastic oxidation, it gives acid with *fewer* carbon atoms.

$$CH_3\text{-}CO\text{-}CH_3 + 2O_2 = CH_3COOH + CO_2 + H_2O.$$

(ii) **Reduction :** Aldehydes on reduction with sodium amalgam and water, yield *primary* alcohols ; acetaldehyde gives ethyl alcohol.

$$CH_3.CHO + H_2 = CH_3.CH_2OH$$

A ketone, on being similarly reduced, gives a *secondary* alcohol ; acetone gives isopropyl or secondary propyl alcohol.

$CH_3CO.CH_3+H_2 = CH_3CH(OH)CH_3$ (isopropyl alcohol)

(iii) **Addition reactions :** (a) Aldehydes and ketones yield the additive compound, cyanhydrin, with hydrocyanic acid, HCN.

$CH_3CHO+HCN = CH_3CH(OH)CN$ (acetalehyde-cyanhydrin).

$(CH_3)_2CO+HCN = (CH_3)_2C(OH)CN$ (acetone-cyanhydrin)

(b) On being shaken with cold saturated solution of sodium bisulphite, $NaHSO_3$, aldehydes and ketones yield bisulphite addition compound.

$CH_3CHO+NaHSO_3 = CH_3CH(OH)SO_3Na$

$(CH_3)_2CO+NaHSO_3 = (CH_3)_2C(OH)SO_3Na$

(c) Acetaldehyde gives acetaldehyde ammonia, a crystalline solid with dry ammonia gas ; $CH_3CHO+NH_3 = CH_3CH(OH)NH_2$

Like acetaldehyde, acetone also forms additive compound with ammonia, but at a low temperature (−65°) only.

$(CH_3)_2CO+NH_3 = (CH_3)_2C(OH)NH_2$ (acetone-ammonia)

But at ordinary temperature acetone forms a complex substance, *diacetone amine*, with ammonia.

(iv) **Reaction with hydroxylamine,** NH_2OH, *hydrazine*, $NH_2.NH_2$, and *phenyl hydrazine*, $NH_2.NHC_6H_5$, etc.

(a) Aldehydes and ketones react with hydroxylamine, giving *oximes*, with elimination of water.

$CH_3CHO+H_2NOH \rightarrow CH_3CH = NOH$ (acetaldoxime) $+H_2O$

$(CH_3)_2CO+H_2NOH \rightarrow (CH_3)_2C = NOH$ (acetoxime) $+H_2O$

(b) Hydrazine reacts similarly with aldehydes and ketones, yielding *hydrazones* with elimination of water.

$CH_3CHO+H_2N.NH_2 \rightarrow CH_3.CH = N.NH_2+H_2O$

$(CH_3)_2CO+H_2N.NH_2 \rightarrow (CH_3)_2C = N.NH_2+H_2O$

(c) Phenyl hydrazine reacts smilarly, giving *phenyl hydrazones* of aldehydes and ketones.

$CH_3CHO+H_2NNHC_6H_5 \rightarrow CH_3CH = NNHC_6H_5+H_2O$

$(CH_3)_2CO+H_2NNHC_6H_5 \rightarrow (CH_3)_2C = NNHC_6H_5+H_2O$

(d) Semicarbazide, $NH_2.NHCONH_2$, reacts with aldehydes and ketones, giving *semicarbazones* which are crystalline and have definite melting points, and hence useful in the identification of aldehydes and ketones.

$CH_3CHO+H_2N.NHCONH_2 \longrightarrow CH_3CH = N.NHCONH_2+H_2O$

$(CH_3)_2CO+H_2N.NHCONH_2 \longrightarrow (CH_3)_2C = N.NHCONH_2+H_2O$

(iv) **Reaction with Grignard reagent :** The aldehyde and ketone form additive compounds with Grignard reagent (such as methyl magnesium bromide, CH_3MgBr), which on hydrolysis yield alcohols. Formaldehyde gives a primary alcohol, acetaldehyde a secondary alcohol and acetone a tertiary alcohol.

$CH_2 = O$ (formaldehyde) $+ CH_3MgBr = CH_3CH_2-OMgBr$
$CH_3CH_2-OMgBr + H.OH = CH_3CH_2OH + Mg(OH)Br$
$CH_3CHO + CH_3MgBr = (CH_3)_2CH-OMgBr$
$(CH_3)_2CH-OMgBr + H.OH = CH_3\text{-}CH(OH).CH_3 + Mg(OH)Br$
$(CH_3)_2CO + CH_3MgBr = (CH_3)_3C-OMgBr.$
$(CH_3)_3\text{-}C\text{-}OMgBr + H.OH = (CH_3)_3C(OH) + Mg(OH)Br$
Tertiary butyl alcohol.

(vi) **Reaction with PCl_5.**—Aldehydes and ketones react with PCl_5, giving dichloroparaffins, but no HCl is evolved. Acetaldehyde gives ethylidene chloride, CH_3CHCl_2, and acetone gives $\beta\beta$-dichloropropane, $CH_3.CCl_2.CH_3$.

$$CH_3CHO + PCl_5 = CH_3CHCl_2 + POCl_3.$$
$$CH_3COCH_3 + PCl_5 = CH_3.CCl_2.CH_3 + POCl_3.$$

The dichloroparaffins thus formed, yield back acetaldehyde and acetone on hydrolysis with hot aqueous alkali.

$$CH_3CHCl_2 + 2NaOH = CH_3CHO + 2NaCl + H_2O$$
$$CH_3.CCl_2.CH_3 + 2NaOH = CH_3COCH_3 + 2NaCl + H_2O$$

(vii) **Reaction with alcohol.**—Aldehydes react with alcohol in presence of HCl gas, giving acetals. Acetone does not give acetal.

$$CH_3CHO + 2HOC_2H_5 = CH_3CH.(OC_2H_5)_2 \text{ (acetal)} + H_2O$$

(viii) **Reaction with caustic soda or potash.**—Acetaldehyde gives a brown resinous mass, known as *aldehyde-resin*, with caustic alkali. But acetone gives no such resin with caustic alkali.

(ix) **Aldol condensation.**—In presence of dilute alkali or aqueous solution of potassium carbonate in the cold acetaldehyde is converted into a syrupy liquid, called *aldol* (which is both aldehyde and alcohol and hence the name *ald* (ehyde-alcoh) *ol*. Aldol is formed by the condensation of two molecules of acetaldehyde. The reaction is called aldol condensation

$$CH_3CHO + CH_3CHO = CH_3CH(OH)CH_2CHO \text{ (aldol)}.$$

The aldol condensation involves the addition of α-hydrogen atoms (i.e., the hydrogen atoms on the carbon atom immediately adjacent to the carbonyl group) on the carbonyl group. If there is no α-hydrogen atoms on the carbon next to carbonyl group, no aldol condensation takes place.

Acetone also undergoes aldol condensation in presence of baryta water, giving diacetone alcohol.

$$(CH_3)_2C{=}O + H_3C-CO-CH_3 = (CH_3)_2.C(OH).CH_2.CO.CH_3$$
Diacetone alcohol.

(x) **Polymerisation.**—Acetaldehyde readily polymerises, but acetone does not.

On adding a drop of concentrated sulphuric acid to a solution of acetaldehyde, the latter polymerises into a colourless, pleasant smelling liquid (b.p. 124°), **paraldehyde,** $(CH_3CHO)_3$. It does not give characteristic aldehyde reactions. It has a cyclic structure.

It is a soporific. By the action of dilute sulphuric acid upon acetaldehyde at low temperature, a solid polymer, **metaldehyde,** $(CH_3CHO)_n$, is formed. It is used as a fuel (meta fuel). Metaldehyde on distillation with dilute sulphuric acid, gives back acetaldehyde. Therefore, polymerisation of aldehydes is a reversible process.

(xi) **Reducing property.**—Aldehydes are readily oxidised and hence are strong reducing agents. (a) Acetaldehyde reduces ammoniacal silver nitrate solution to metallic silver, on warming.

$$CH_3CHO + Ag_2O = CH_3COOH + 2Ag\ ;$$

(b) Acetaldehyde reduces Fehling's solution on boiling, giving a red precipitate of cuprous oxide.

$$CH_3CHO + 2CuO = CH_3COOH + Cu_2O.$$

Fehling's solution contains copper sulphate, caustic soda and sodium potassium tartrate (Rochelle salt), and is deep blue in colour.

Acetone has no reducing property. It does not reduce ammoniacal silver nitrate or Fehling's solution.

(xii) **Action on Schiff's reagent.**—Acetaldehyde gives purple colour with Schiff's reagent (which is magenta solution made colourless with sulphur dioxide) in the cold. Acetone does not ordinarily restore the colour of Schiff's reagent.

(xiii) **Haloform reaction.**—With bleaching powder solution or chlorine and caustic soda solution both acetaldehyde and acetone give chloroform. Similarly, with bromine or iodine and caustic soda, they give bromoform, $CHBr_3$, and iodoform, CHI_3. This is known as *haloform reaction*.

$$CH_3CHO + 2NaOCl = CCl_3.CHO + 3NaOH$$
$$CCl_3CHO + NaOH = CHCl_3 + HCOONa$$

Acetone reacts similarly.

Uses of acetaldehyde—Paralydehyde is a hypnotic. Metaldehyde is used as a fuel. Acetaldehyde is used in the preparation of acetic acid, ethyl alcohol, acetic anhydride, ethylacetate and aldol.

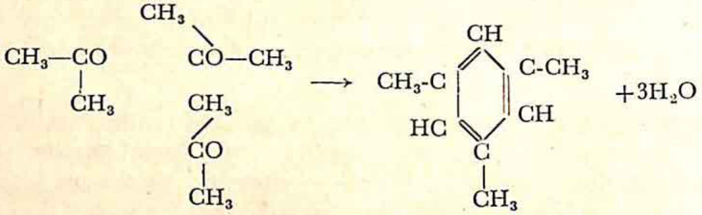
Test for acetaldehyde.—(i) Acetaldehyde reduces ammoniacal silver nitrate and Fehling's solution, and restores colour of Schiff's reagent.

(ii) Acetaldehyde solution gives a blue colour on the addition of aqueous sodium nitroprusside and piperidine.

(iii) A cherry-red colour devlops, on adding sodium nitroprusside solution and an excess of aqueous caustic soda to acetaldehyde solution.

Polymerisation.—When acetylene is passed through a red-hot tube, benzene is formed : $3C_2H_2 \longrightarrow C_6H_6$. Such a reaction in which a simple substance is changed into a complex one of the *same empirical formula* but having a molecular weight equal to several multiples of the parent substance, is known as *polymerisation*. The complex substance formed is the *polymer* of the original substance which is called the *monomer*. Polymer has the same empirical formula as the monomer but different molecular formula. Benzene is a trimer of acetylene. Polymerisation is usually reversible, as in the case of polymers of acetaldehyde but this need not be so. Ethylene on polymerisation gives the synthetic resin *polythene*.

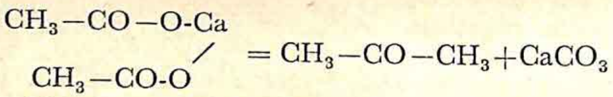
Condensation.—When acetone is distilled with concentrated sulphuric acid, it yields mesitylene (trimethyl benezene), a liquid boiling at 163°. Three molecules of acetone interact, with elimination of water and forming mesitylene.



Such a process in which two or more molecules of the same or different substances combine, usually, but not always, with elimination of water, alcohol, HCl, etc., is known as *condensation*, and the substance formed is the *condensation product*—the combination is caused by the union of carbon atoms and hence the condensation product is of stable character. Mesitylene is formed with elimination of water, but in the formation of aldol nothing is eliminated. But in both cases new linkage between carbon atoms of the original molecules develop, and consequently they can not be easily split up into the original molecules.

Acetone, dimethyl ketone, $CH_3\text{-}CO.CH_3$, occurs in traces in normal urine, but in the case of diabetic patients, the quantity increases. It also occurs in trace in blood.

Acetone is made commercially : (i) **by dry distillation of calcium acetate.** The method is also suitable for laboratory preparation.



$$\begin{matrix} CH_3-CO-O\text{-}Ca \\ CH_3-CO\text{-}O \diagup \end{matrix} = CH_3-CO-CH_3+CaCO_3$$

Dry calcium acetate (30 g.) is heated first slowly and then strongly in a retort attached to a condeser and receiver (fig. 89). The distillate is crude acetone. It is shaken with saturated solution of sodium bisulphite, when crystalline acetone-bisulphite is deposited. This is filtered and decomposed by distillation with sodium carbonate solution. The acetone passes over. It is dried over calcium chloride and redistilled to get pure acetone.

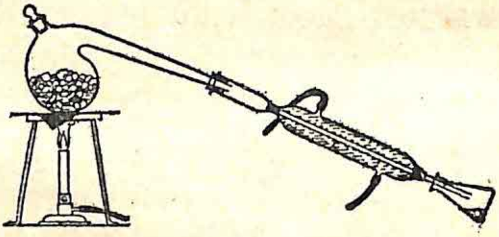


Fig. 89.

$$CH_3.CO.CH_3+NaHSO_3 \leftrightharpoons (CH_3)_2.C(OH).SO_3Na$$

$$2(CH_3)_2.C(OH).SO_3Na+Na_2CO_3$$
$$= 2(CH_3)_2CO+2Na_2SO_3+H_2O+CO_2$$

The calcium acetate (the grey acetate of lime of commerce) is obtained by neutralising the acetic acid of the pyroligneous acid with milk of lime. Acetone is also recovered from crude wood spirit by fractional distillation.

(ii) by passing acetic acid vapour over manganous oxide, MnO, catalyst at 300° :

$$2CH_3COOH = CH_3COCH_3 + CO_2 + H_2O$$

(iii) by oxidation of isopropyl alcohol by means of air in presence of heated copper catalyst, or by dehydrogenation by passing over heated copper.

$$CH_3.CH(OH).CH_3 + O = CH_3.COCH_3 + H_2O$$

Isopropyl alcohol, $CH_3.CH(OH).CH_3$, is made by absorption of propylene, $CH_3CH = CH_2$, (from cracked petroleum) in concentrated H_2SO_4, and then hydrolysing the product by heating with dilute H_2SO_4.

$$CH_3\text{-}CH = CH_2 + H_2SO_4 = CH_3.CH(HSO_4)CH_3$$

$$CH_3\text{-}CH(HSO_4).CH_3 + H_2O = CH_3CH(OH).CH_3 + H_2O$$

(iv) by fermentation of starch of maize and rice **(Weizmann process)** in presence of an organism (*Fernbach's bacillus*) which converts the starch mainly into a mixture of butyl alcohol and acetone. The acetone is separated by fractional distillation.

(v) by passing a mixture of ethyl alcohol vapour and steam over a heated catalyst containing iron and calcium :

$$2CH_3CH_2OH + H_2O = CH_3COCH_3 + 4H_2 + CO_2.$$

(vi) by passing a mixture of acetylene and steam over heated zinc oxide catalyst :

$$2C_2H_2 + 3H_2O = CH_3COCH_3 + 2H_2 + CO_2.$$

Properties.—Acetone is a colourless liquid with a pleasant smell (b.p. 56.5°). It is soluble in water, alcohol and ether. Its sp. gr. is 0.792 at 20°.

There are many common reactions of acetone and acetaldehyde ; they have been discussed together under acetaldehyde.

Uses.—Acetone is used as a *solvent* for nitrocellulose in making cordite, and for storing acetylene. It is used in making chloroform, iodoform and sulphonal (a hypnotic), and in spinning cellulose acetate rayon. **Chloretone**, a specific against sea-sickness, is made by the action of potash on a mixture of acetone and chloroform.

$$(CH_3)_2.CO + CHCl_3 = (CH_3)_2.C(OH).CCl_3. \quad \text{(chloretone).}$$

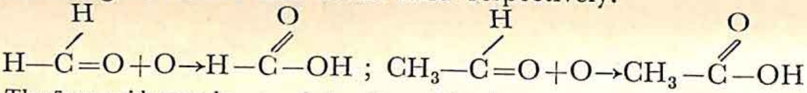
Tests.—(i) Like ethyl alcohol acetone gives iodoform reaction with iodine and caustic soda solution. But unlike ethyl alcohol, acetone also gives an iodoform reaction with iodine and aqueous *ammonia* (in place caustic soda). Hence acetone is distinguished from ethyl alcohol.

(ii) A freshly prepared solution of sodium nitroprusside on being added to acetone and then made alkaline with caustic soda, develops an orange red colour (*Legal's test*).

ORGANIC ACIDS AND ESTERS

Fatty acids.—Formic acid, HCOOH, and acetic acid, CH_3COOH are the first two members of a series of homologous saturated monobasic acids, known as *fatty acids*. They are so called as two of the higher members—*palmitic acid* and *stearic acid*—are present in animal fats. All acids of the series have the general formula $\text{R-}\overset{\text{O}}{\overset{/\!/}{\text{C}}}\text{-OH}$, where R is an alkyl group, except formic acid which has the formula $\text{H-}\overset{\text{O}}{\overset{/\!/}{\text{C}}}\text{-OH}$. The carboxylic group $-\overset{\text{O}}{\overset{/\!/}{\text{C}}}\text{-OH}$, is the characteristic of all organic acids. The fatty acids contain one —COOH group and are, therefore, mono carboxylic acids. It is the hydrogen atom of the —COOH group which is replaceable by metals, forming salts.

Formaldehyde, H-CHO, and acetaldehyde, CH_3-CHO, on oxidation give formic and acetic acid respectively.



$$\text{H}-\overset{\text{H}}{\overset{/}{\text{C}}}=\text{O}+\text{O}\rightarrow\text{H}-\overset{\text{O}}{\overset{/\!/}{\text{C}}}-\text{OH}\ ;\ \text{CH}_3-\overset{\text{H}}{\overset{/}{\text{C}}}=\text{O}+\text{O}\rightarrow\text{CH}_3-\overset{\text{O}}{\overset{/\!/}{\text{C}}}-\text{OH}$$

The fatty acids may be regarded as formed by the stepwise oxidation of paraffins. The sequence of the steps are :

Paraffin ⟶ Primary alcohol ⟶ Aldehyde ⟶ Fatty acid

$CH_4 \longrightarrow H.CH_2OH \longrightarrow H.CHO \longrightarrow H.COOH$ (formic acid)

$CH_3\text{-}CH_3 \longrightarrow CH_3.CH_2OH \longrightarrow CH_3.CHO \longrightarrow CH_3.COOH$ (acetic acid)

Acetic acid, CH_3COOH, has long been known under the name of vinegar, and is formed when beer gets sour. The name 'acid' is derived from Latin *acetum*, meaning vinegar.

Acetic acid is *formed* as follows : (i) Hydrolysis of methyl cyanide by heating with aqueous alkali or strong mineral acid.

$$CH_3CN+2H_2O = CH_3COOH+NH_3$$

In presence of alkali, ammonia is evolved and acetate is formed, but in acid medium free acetic and ammonium salt are formed.

(ii) Oxidation of ethyl alcohol by prolonged heating with potassium dichromate and sulphuric acid, or by passing a mixture of the alcohol vapour and air over platinum black at 70°. Acetaldehyde is similarly oxidised.

$$CH_3CH_2OH+O = CH_3CHO+H_2O\ ;\ CH_3CHO+O = CH_3COOH$$

(iii) Sodium methoxide, CH_3ONa, is heated in an atmosphere of carbon monoxide to about 180°. $CH_3.ONa+C=O \longrightarrow CH_3-COONa$

Acetic acid is commonly available in two forms—concentrated acetic acid, also called *glacial acetic acid*, and dilute acetic acid, known as *vinegar*. Their methods of preparation are different.

Glacial acetic acid is made : (a) **From pyroligneous acid.**—The pyroligneous acid is neutralised with milk of lime, and methyl alcohol and acetone are distilled off—the solution of calcium acetate is then evaporated to dryness. The dry calcium acetate (grey acetate of lime) is distilled with concentrated sulphuric acid—the distlilate contains about 50% acetic acid.

$$(CH_3COO)_2Ca+H_2SO_4 = CaSO_4+2CH_3COOH$$

This is neutralised with caustic soda solution and the solution is evaporated to dryness. The dry sodium acetate thus formed is again distilled with concentrated H_2SO_4—the distillate is glacial acetic acid.

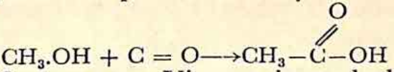
$$2CH_3COONa+H_2SO_4=2CH_3COOH+Na_2SO_4$$

Any water still present is removed by cooling the acid in ice, when pure acetic acid alone solidifies as colourless ice-like (glacial) mass (leaving the water behind), and hence the name *glacial* acetic acid. Pure acetic acid freezes at 16.7° and boils at 119°.

(b) **From acetylene.**—Acetaldehyde is first made by bubbling acetylene into hot 20% sulphuric acid containing a little mercuric sulphate, at about 70°. The acetaldehyde is then oxidised by air at about 60° in presence of manganous acetate which acts as a catalyst. The glacial acetic acid is made by fractional distillation.

$$CH\equiv CH+H_2O = CH_3CHO \ ; \ CH_3CHO+O = CH_3COOH$$

Acetic acid can also be obtained by interaction between CH_3OH and CO under high pressure and temperature in presence of catalyst.



$$CH_3.OH + C = O \longrightarrow CH_3-\overset{\overset{O}{/\!/}}{C}-OH$$

Preparation of vinegar.—Vinegar is made by fermentation of weak ethyl alcohol with a microorganism *bacterium aceti* (often called *mother of vinegar*) in presence of air. Air oxidises the alcohol to acetic acid under the influence of an enzyme, present in the organism.

$$CH_3CH_2OH+O \longrightarrow CH_3COOH+H_2O$$

On exposure to air (in which the vinegar organism is always present), therefore, beer and a weak wine gradually go sour, owing to the formation of acetic acid. Strong wines (containing more than 15% alcohol) such as port and sherry, do not go sour, as the organism cannot survive in strong alcohol.

In the **quick vinegar process** a dilute solution (5-7 per cent) of ethyl alcohol is allowed to trickle over a mass of beech wood shavings contained in a tall wooden vat ; the shavings have previously been soaked in vinegar (which contains the vinegar organism) and are, therefore, covered with the mother of vinegar. Air circulates through the vat and oxidises the alcohol as it trickles down to acetic acid. A plantiful supply of air is essential ; with too little air acetaldehyde is formed. The temperature is kept at 35°. The liquid running out below contains 4.6% acetic acid, but by allowing the liquid to trickle a few times through the vat, vinegar containing 14 per cent acetic acid may be made. Vinegar is never used to prepare glacial acetic acid.

Properties.—Acetic is a colourless liquid (b.p. 119°) with a pungent smell (smell of vinegar) and a sharp sour taste. It is corrosive and blisters the skin. At 16.7° it freezes to an ice-like (glacial) mass, called *glacial acetic acid*. It is soluble in water, alcohol and ether. Acetic acid is a useful solvent for many organic compounds, as it is comparatively inert towards oxidising agents.

Reactions :—(i) **Salt formation :** Acetic acid is a weak acid, weaker than the mineral acids HCl, HNO_3 and H_2SO_4. It is also weaker than formic acid. It is a monobasic acid and forms salts known as *acetates*, by usual methods :

$$CH_3COOH+NaOH = CH_3COONa+H_2O$$

$$2CH_3COOH+Zn = (CH_3COO)_2Zn+H_2$$

(ii) **Ester formation.**—When acetic acid is heated with alcohol, e.g. ethyl alcohol, in presence of a dehydrating agent, usually concentrated H_2SO_4 or HCl gas, an *ester* and water are formed :

$$\text{Acid}+\text{alcohol} \rightleftharpoons \text{ester}+\text{water}$$

$$CH_3COOH+HOC_2H_5 \rightleftharpoons \underset{\text{Ethylacetate}}{CH_3COOC_2H_5}+H_2O$$

The reaction is *reversible*, and the reverse action is known as *hydrolysis*. The dehydrating agents absorb the water formed, and thereby prevent the hydrolysis of the ester.

(iii) **Action of PCl_5.**—Phosphorus pentachloride acts on acetic acid, forming acetyl chloride, CH_3COCl,—the OH group of the acid is replaced by chlorine.

$$CH_3CO.OH+PCl_5 = CH_3COCl+POCl_3+HCl$$

(iv) **Action of chlorine.**—By direct action of chlorine the hydrogen atoms of the methyl group, $-CH_3$, in CH_3COOH is replaced by chlorine in stages, forming monochloro-, dichloro-, and trichloro- acetic acids.

$$CH_3.COOH+Cl_2 = CH_2Cl.COOH+HCl$$

$$CH_2Cl.COOH+Cl_2 = CHCl_2COOH+HCl$$

$$CHCl_2.COOH+Cl_2 = CCl_3.COOH+HCl$$

The action is accelerated by sunlight or in presence of red phosphorus or iodine. Bromine reacts similarly, but iodine is without direct action upon acetic acid.

Monochloroacetic acid, $CH_2ClCOOH$, is important in organic synthesis, as the chlorine atom introduced in the CH_3-group shows the reactivity of an alkyl halide :

(a) **Hydrolysis** with moist silver oxide replace the chlorine atom by OH group, giving hydroxyacetic acid or glycollic acid :

$$CH_2ClCOOH+AgOH = CH_2(OH).COOH+AgCl$$

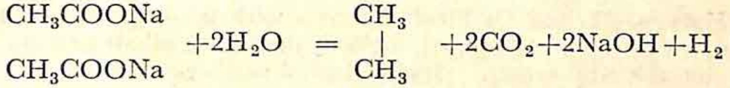
(b) Alcoholic ammonia gives amino-acetic acid or glycine :

$$CH_2ClCOOH+NH_3 = CH_2(NH_2).COOH+HCl$$

(c) Alcoholic potassium cyanide gives cyanacetic acid.

$$\underset{\text{Potassium chloroacetate}}{CH_2Cl.COOK}+KCN = \underset{\text{potassium cyanacetate}}{CH_2(CN).COOK}+Cl$$

(v) **Formation of ethane.**—An aqueous solution of sodium (or potassium) acetate yields, on electrolysis, a mixture of ethane and CO_2 at the anode, and caustic soda (or potash) and hydrogen at cathode. This is *Kolbe's method.*



$$\begin{array}{l} CH_3COONa \\ CH_3COONa \end{array} + 2H_2O = \begin{array}{c} CH_3 \\ | \\ CH_3 \end{array} + 2CO_2 + 2NaOH + H_2$$

(vi) **Formation of methane.**—Sodium acetate on heating with sodalime, gives methane. $CH_3COONa + NaOH = CH_4 + Na_2CO_3$

(vii) **Formation of acetamide.**—Ammonium acetate on heating gives acetamide, CH_3CONH_2.

$$CH_3COONH_4 = CH_3CONH_2 + H_2O$$

(viii) **Formation of acetaldehyde and acetone.**—A mixture of calcium acetate and calcium formate yields acetaldehyde, on heating. Heating calcium acetate alone gives acetone.

(ix) **Formation of acetic anhydride.**—A mixture of sodium acetate and acetyl chloride gives acetic anhydride, on heating.

$$CH_3CO.ONa + ClCOCH_3 = CH_3CO.O.COCH_3 + NaCl$$

The reactions of acetic acid are typical of the fatty acids.

Uses of acetic acid—Acetic acid is used : (i) in the preparation of acetates, acetic anhydride, acetyl chloride, acetone and ethyl acetate, (ii) in making cellulose acetate rayon, (iii) in coagulating rubber latex, and (iv) in curing meat and fish. It is an important laboratory reagent and also a solvent. A mixture of glacial acetic acid and chromic oxide, CrO_3, is a powerful oxidising agent.

The acetates.—The acetates (the normal salts of acetic acid) are mostly crystalline solids which are soluble in water. Sodium and potassium acetates are often used in organic reactions to convert a mineral acid into weaker organic acid.

$$CH_3COONa + HCl \rightleftharpoons CH_3COOH + NaCl.$$

Basic acetate of copper (*verdigris*) is a green pigment. Basic lead acetate, called *sugar of lead* because of its sweet taste, is used in medicine. *Paris green* (a mixture of copper acetate and copper arsenite) is an insecticide. Acetates of iron and aluminium are used as *mordants* (i.e., substances which serve to attach the dye 'fast' to the cloth) in dyeing cotton cloth. The cloth is steeped in iron (or aluminium) acetate solution and then steamed, when the acetates are hydrolysed—the acetic acid is driven off and the hydroxides of Fe and Al are deposited on the fibre, where they combine with the dye and finally fix it.

Tests for acetic acid.—Dry tests : Use solid sodium acetate.

Reagent	Acetic acid
(i) Dilute H_2SO_4. Warm	Smell of vinegar
(ii) Ethyl alcohol + conc. H_2SO_4; Warm	Fruity smell of ethyl acetate
(iii) Arsenious oxide, Heat *	Nauseating smell of cacodyl oxide.

* **Cacodyl oxide test.**—On heating *dry* acetate with a little arsenious oxide, As_2O_3, a nauseating smell of cacodyloxide is produced.

Wet tests : Use neutral aqueous solution of sodium acetate.

Reagent	Acetic acid
(i) $FeCl_3$ solution	Deep red colour
(ii) $AgNO_3$ solution	White precipitate ; does not blacken on heating.

Esters.—When an alcohol reacts with an organic or inorganic acid, an ester and water are formed, just as an alkali acts on an acid to give salt and water. Acid+alcohol ⇋ Ester+water

$$\underset{\text{Acetic acid}}{CH_3COOH}+\underset{\text{Ethyl alcohol}}{C_2H_5OH} \rightleftharpoons \underset{\text{Ethyl acetate}}{CH_3COOC_2H_5}+\underset{\text{water}}{H_2O}$$

$$(\text{cf. } CH_3COOH+NaOH \rightleftharpoons CH_3COONa+H_2O).$$

$$C_2H_5OH+\underset{\text{Nitric acid}}{HO.NO_2} = \underset{\text{Ethyl nitrate}}{C_2H_5ONO_2}+H_2O.$$

Ester may be looked upon as acids in which the acid hydrogen, i.e., replaceable hydrogen atom, has been changed for an alkyl group, just as a salt is formed by replacing the acid hydrogen by a metal. But it must be made clear that alcohols are not bases, nor are esters salts,

Ethyl acetate, $CH_3COOC_2H_5$ is made : (i) by heating ethyl alcohol and acetic acid in presence of concentrated sulphuric acid which acts as a dehydrating agent.

Preparation.—Equal volumes of ethyl alcohol and concentrated sulphuric acid are taken in a distilling flask fitted with a condenser and a receiver, and the mixture heated on a oil bath to 140°. A mixture of equal volumes of glacial acetic acid and ethyl alcohol is run in from a tap funnel at the same speed as the liquid distils over into the receiver. The distillate contains ethyl acetate and some alcohol, acetic acid and water. It is shaken with sodium carbonate solution when the acid is neutralised. The aqueous layer is separated from the upper oily layer of the ester. The oil is then shaken with sodium chloride solution when alcohol passes into the aqueous layer, and is separated. The oil is then dried over calcium chloride and distilled from a water bath. Ethyl acetate boils at 77°.

(ii) by boiling under reflux (fig. 90) a mixture of ethyl alcohol (which has been saturated with hydrogen chloride gas) and acetic acid for about half an hour and pouring the product into sodium chloride solution (Fischer-Speier method). The ester separates as an oil, which is purified as above. HCl acts partly as a dehydrating agent and partly as a catalyst.

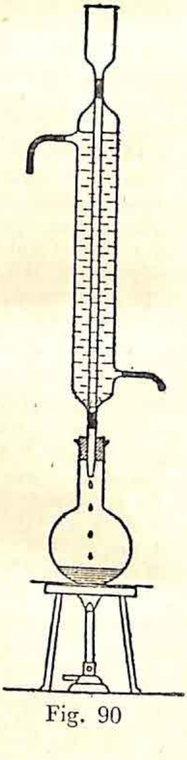


Fig. 90

(iii) by the action of ethyl iodide on silver acetate.

$$CH_3COOAg+IC_2H_5 = CH_3COOC_2H_5+AgI.$$

(iv) by the action of acetyl chloride or acetic anhydride on ethyl alcohol.

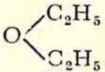
$$CH_3COCl+HOC_2H_5 = CH_3COOC_2H_5+HCl.$$

Ethyl acetate is now made commercially from acetaldehyde in presence of aluminium ethylate as a catalyst.

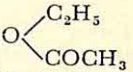
$$2CH_3CHO = CH_3COOC_2H_5$$

Properties.—Ethyl acetate is a colourless neutral liquid with a pleasant, fruity smell, b.p. 77°. It is lighter than water (sp. gr. 0.9 at 20°) and sparingly soluble in it. It is soluble in alcohol and ether.

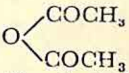
In point of structure and in chemical behaviour it stands between very stable ether and unstable acetic anhydride.


$O(C_2H_5)_2$

Ether


$O(C_2H_5)(COCH_3)$

Ethyl acetate


$O(COCH_3)_2$

Acetic anhydride

Reactions.—(i) **Hydrolysis :** Ethyl acetate is slowly decomposed by hot water into ethyl alcohol and acetic acid, but much more rapidly in presence of mineral acids or caustic alkali.

$$CH_3COOC_2H_5+H_2O \rightleftharpoons CH_3COOH+C_2H_5OH$$
$$CH_3COOC_2H_5+NaOH = CH_3COONa+C_2H_5OH.$$

Hydrolysis of an ester in presence of alkali, giving salt of the acid and alcohol, is known as **saponification.**

(ii) **Ammonolysis :** Ammonia reacts, giving acetamide and ethyl alcohol. $CH_3COOC_2H_5+HNH_2 = CH_3CONH_2+C_2H_5OH$

(iii) **Alcoholysis :** It reacts with another alcohol, e.g., CH_3OH, giving ester of the added alcohol, e.g., methyl acetate, CH_3COOCH_3.

$$CH_3COOC_2H_5+HOCH_3 = CH_3COOCH_3+C_2H_5OH$$

(iv) **Reduction to alcohol :** It is reduced to alcohol (a) with nascent hydrogen by the action of sodium and alcohol [**Bouveault—Blanc reaction**], (b) by the action of hydrogen at high pressure (200 atmospheres) and temperature (250°) in presence of copper chromite

$$CH_3COOC_2H_5+2H_2 = CH_3CH_2OH+C_2H_5OH$$

Ester reduction offers a method to convert a fatty acid, R.COOH, into a primary alcohol, $R.CH_2OH$; in the above instance CH_3COOH (as ethyl acetate) is reduced to CH_3CH_2OH.

(v) **Reaction with PCl_5** yields acetyl chloride and ethyl chloride.

$$CH_3COOC_2H_5+PCl_5 = CH_3COCl+POCl_3+C_2H_5Cl$$

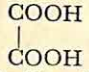
An ester is gnerally **identified** by separating and identifying the alcohol and acid formed on hydrolysis of an ester with hot aqueous alkali.

Ethyl acetate is used as a solvent for nitro-cellulose in the preparation of photographic films, and in essences. A good stimulent, it finds use in medicine.

Many esters occur in fruits, flowers and other parts of plants, and it is to their presence generally that the sweet smell of the part is due. On account of their sweet scent they are prepared artificially and used as substitutes for natural perfumes and fruit essences. Ethyl formate is used as a constituent of artificial rum flavour. Ethyl butyrate occurs in pineapples. Amyl butyrate possesses an apricot flavour. Octyl acetate is present in oranges. Amyl acetate has a smell of pears and is used in making artificial banana oil. Many esters, such as amyl acetate and butyl acetate, are used as solvents, mainly for lacquers.

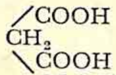
The dicarboxylic acids contain two -COOH groups and hence two replaceable hydrogen atoms ; they are therefore, dibasic acids.

The examples are:



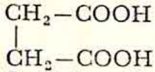
$$\begin{matrix}COOH\\ |\\ COOH\end{matrix}$$

Oxalic acid



$$CH_2(COOH)_2$$

Malonic acid



$$\begin{matrix}CH_2-COOH\\ |\\ CH_2-COOH\end{matrix}$$

Succinic acid

and so on.

Oxalic acid, HOOC-COOH.—Wood sorrel and other plants contain potassium hydrogen oxalate, sometimes called *salts of sorrel.* Calcium oxalate crystals are found in certain plant cells.

Preparation.—(i) In the laboratory oxalic acid is made by gently heating cane sugar with concentrated nitric acid.

$$C_{12}H_{22}O_{11}+9O_2 = 6(COOH)_2+5H_2O$$

Strong nitric acid (200 c.c.) is taken in a large flask and heated on water bath. The flask is removed to a fume cupboard and 50 gms. of cane sugar added. Torrents of brown fumes are evolved. After the reaction has ceased, the solution is concentrated in a basin on a water bath. Large crystals of oxalic acid separate on cooling.

(ii) Commercially, oxalic acid is made from : (a) Pine sawdust by heating (avoiding charring) with caustic soda in iron pans to about 250°—fused alkali oxidises cellulose (in the sawdust) into sodium oxalate. The fused mass is extracted with water. The solution contains sodium oxalate, which on boiling with milk of lime precipitates calcium oxalate. The calcium oxalate is separated and decomposed by calculated amount of dilute H_2SO_4.

$$Ca(COO)_2+H_2SO_4 = CaSO_4+(COOH)_2$$

The $CaSO_4$ is filtered off. The filtrate on concentration and cooling, gives crystals of oxalic acid.

(b) Sodium formate by heating to 350°-400° when sodium oxalate is formed. Oxalic acid is made from the sodium oxalate in the same way as in (a) above.

$$2H.COONa = H_2 + (COONa)_2.$$

Properties.—(i) Oxalic acid crystallises from water in colourless hydrated prisms, $(COOH)_2$, $2H_2O$. The crystals of dihydrate lose water of crystallisation at 100° and become anhydrous. But at higher temperatures it decomposes into formic acid and carbon dioxide.

$$HOOC\text{-}COOH = H.COOH+CO_2$$

It is soluble in water and alcohol, but only sparingly in ether.

(ii) Heating with conc. H_2SO_4 decomposes oxalic acid, evolving CO and CO_2. $HOOC\text{-}COOH = H_2O+CO_2+CO.$

(iii) It is a dibasic acid and forms normal salts, e.g. potassium oxalate, $K_2C_2O_4$, soluble in water, and acid salts e.g., potassium hydrogen oxalate, KHC_2O_4, which is less soluble.

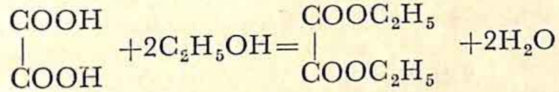
(iv) Oxalic acid rapidly decolorises potassium permanganate solution in presence of dilute sulphuric acid, on warming, and is thereby oxidised to CO_2 and water. The reaction is used in volumetric analysis.

$$2KMnO_4+3H_2SO_4+5H_2C_2O_4 = K_2SO_4+2MnSO_4+8H_2O+10CO_2$$

(v) Reaction with PCl_5 gives oxalyl chloride, $(COCl)_2$, b.p. 64°.

$$HOOC\text{-}COOH + 2PCl_5 = ClOC\text{-}COCl + 2POCl_3 + 2HCl$$

(vi) Esters are made by distilling oxalic acid with alcohol. Ethyl alcohol gives ethyl oxalate, a liquid, b.p. 186°.



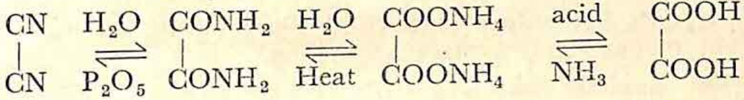
$$\begin{array}{l}COOH\\ |\\ COOH\end{array} + 2C_2H_5OH = \begin{array}{l}COOC_2H_5\\ |\\ COOC_2H_5\end{array} + 2H_2O$$

Methyl oxalate is a solid, m.p. 51°.

(vii) Ammonium oxalate on heating gives oxamide, $(CONH_2)_2$.

$$H_4NOOC\text{-}COONH_4 = H_2NOC\text{-}CONH_2 + 2H_2O$$

(viii) On heating with P_2O_5, oxamide gives off cyanogen, $(CN)_2$, a poisonous gas. Cyanogen is the nitrile of oxalic acid, as it yields oxamide and finally oxalic acid on acid hydrolysis.



$$\begin{array}{c}CN\\ |\\ CN\end{array} \underset{P_2O_5}{\overset{H_2O}{\rightleftharpoons}} \begin{array}{c}CONH_2\\ |\\ CONH_2\end{array} \underset{Heat}{\overset{H_2O}{\rightleftharpoons}} \begin{array}{c}COONH_4\\ |\\ COONH_4\end{array} \underset{NH_3}{\overset{acid}{\rightleftharpoons}} \begin{array}{c}COOH\\ |\\ COOH\end{array}$$

(ix) A neutral solution of an oxalate gives a white precipitate of calcium oxalate with $CaCl_2$ solution ; the precipitate is insoluble in acetic acid. Reactions (ii), (iv) and (ix) are used as *tests* for oxalic acid.

Oxalic acid and its salts are poisonous.

Uses of oxalic acid.—Oxalic acid is used in printing and dyeing, in making inks and metal polish, in removing ink stains, and for bleaching straws for hats. *Potassium quadro oxalate*, $KHC_2O_4.H_2C_2O_4.2H_2O$, also known as *salts of sorrel or lemon*, is used to remove ink stains and ink moulds. *Potassium ferrous oxalate*, $K_2Fe(C_2O_4)_2H_2O$ is a photographic developer.

The hydroxy acids are compounds which combine the properties of alcohols and acids, i.e., they contain both hydroxyl and carboxyl groups e.g., hydroxy acetic acid (glycollic acid),

$$CH_2(OH).COOH.$$

Citric acid, $C_6H_8O_7$, occurs free in citrus fruits (and hence the name) such as lime, lemon, tomato and orange. Scheele isolated the acid from lemon juice in 1784.

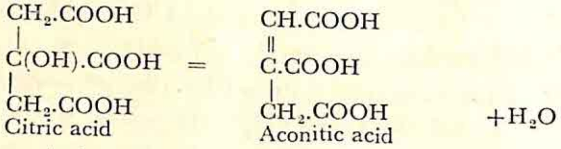
Citric acid, is made from lemon juice, which contain 7-8% of the acid. The juice is boiled to coagulate the protein which is removed by decantation ; the decanted liquid is then neutralised with milk of lime or calcium carbonate and *boiled*, when calcium citrate is precipitated. The precipitate is separated and decomposed with calculated amount of dilute H_2SO_4. The insoluble $CaSO_4$ is filtered off—the filtrate gives crystals of citric acid on concentration and cooling.

Citric acid is also made by fermentation of glucose or cane sugar by the action of certain molds or fungi, such as *Aspergillus niger* or *citromycetes*. A dilute solution of glucose or cane sugar molasses (containing 10—15 per cent sugar) is fairly acidified and kept with the ferment at about 30° in shallow, open aluminium pans—in about a week's time or so the sugar is converted into citric acid with evolution of CO_2.

The liquid is neutralised with milk of lime and boiled to precipitate the calcium citrate from which the citric acid is obtained, as above.

Properties.—(i) Citric acid forms large transparent crystals, $C_6H_8O_7.H_2O$. The crystals melt at 100°, but the anhydrous acid at 153°. It is soluble in water and alcohol, but not in ether.

(ii) When heated to 175°, it loses a molecule of water, forming aconitic acid.



$$\begin{array}{l} CH_2.COOH \\ | \\ C(OH).COOH \\ | \\ CH_2.COOH \\ \text{Citric acid} \end{array} = \begin{array}{l} CH.COOH \\ \| \\ C.COOH \\ | \\ CH_2.COOH \\ \text{Aconitic acid} \end{array} + H_2O$$

Citric acid is a monohydroxy-tricarboxylic acid

(iii) It is optically inactive, as it contains no asymmetric carbon atom in the molecule.

(iv) It does not reduce ammonical silver nitrate on warming, but slight reduction takes place on boiling.

(v) On carefully warming with concentrated sulphuric acid, it decomposes into water, CO, and acetone dicarboxylic acid,

$$HOOC\text{-}CH_2-CO-CH_2-COOH.$$

(vi) A neutral solution of a citrate gives a white precipitate of calcium citrate on *boiling* with $CaCl_2$ solution. (*a test for citric acid*). Calcium citrate is soluble in cold but insoluble in boiling water.

Uses.—Citric acid is used in making lemonades and as a mordant in dyeing. Ferric-ammonium citrate is used in medicine.

XXVIII

AROMATIC HYDROCARBONS

Aromatic hydrocarbons.—A small group of plant products such as gum benzoin, tolu balsam, oil of bitter almonds and oil of winter-green, etc., was originally classified as *aromatic* because of the fragrant smell or *aroma* they all possess in common.

The aromatic compounds contain a higher percentage of carbon than the corresponding aliphatic hydrocarbons and burn with a smoky flame. Thus, benzene, C_6H_6, the simplest aromatic hydrocarbon, contains 93.6 per cent, whereas hexane, C_6H_{14}, contains 83.7 per cent carbon.

Most of the simple aromatic compounds contain at least *six* carbon atoms. The more complex aromatic compounds may be converted by the action of appropriate reagents into the simplest aromatic hydrocarbon benzene, C_6H_6 or its derivatives. But any attempt to convert an aromatic compound into compounds with fewer carbon atoms than six (as in benzene) disrupts the entire molecule. Benzene is, therefore, regarded as the parent substance of all aromatic compounds. Compounds derived from or closely related to benzene are now called aromatic to distinguish them from aliphatic compounds. They are cyclic or ring compounds *containing at least one benzene ring*.

Coal tar.—Coal tar is the principal source of benzene and many other aromatic compounds such as toluene, xylene, naphthalene and carbolic acid etc. Synthetic organic dyestuffs are aromatic compounds. The discovery of the first synthtic coal tar colour *mauve* by W. H. Perkin in 1856 gave a stimulus to the study of coal tar products which largely helped the development of aromatic chemistry.

The dry distillation of coal at high temperatue (1000-1400°) yields coal tar (about 5 per cent of coal), ammoniacal liquour (8 per cent), coal gas (70 per cent) and coke (17 per cent).

Coal tar is a thick, black oily liquid (sp. gr. 1.1-1.2) with unpleasant smell. Water is removed from the tar by heating and the tar is then distilled in iron retorts—the distillate is collected in a number of fractions in separate receivers according to specific gravity or temperature at which the fraction is collected. The fractions are :

Temperature range	Number of fractions	Sp. gr.	Yield by volume
Upto 170°	Light oil or crude naphtha	0.970	2-8 per cent
170° to 230°	Middle oil or carbolic oil	1.005	8-10 ,, ,,
230° to 270°	Heavy oil or creosote oil	1.033	8-10 ,, ,,
270° to 360°	Green oil or anthracene oil	1.088	16-20 ,, ,,
—	Pitch (left in still)	—	55-60 ,, ,,

These fractions are then worked up and separated into their constituents. The major constituents of different fractions are :

Light oil	Middle oil	Heavy oil	Green oil
Benzene, C_6H_6 Tolune, $C_6H_5.CH_3$ Xylene, $C_6H_4.(CH_3)_2$	Phenol, C_6H_5OH Naphthalene, $C_{10}H_8$	Cresols, $C_6H_4(CH_3)OH$	Anthracene, $C_{14}H_{10}$ Phenanthrene, $C_{14}H_{10}$

The creosote oil is not separated into its constituents and is used as such for preserving timber. The pitch finds uses in roofing and road-making. Naphthalene, a white crystalline solid, m.p. 79°, is used in making dyestuffs (alizarin) and solvents (tetralin and decalin). It acts as a vermin-killer and a mild antiseptic, and is commonly sold as balls for use as a protection against moths. Anthracene, a colourless solid with a bluish fluorescence, m.p. 216°, is used in making dyes. The coal tar hydrocarbons are the starting point for the synthesis of many dyes, drugs, photographic developers, explosives, flavours and perfumes.

Isolation of benzene.—The crude light oil is re-distilled and the distillate below 70° is rejected. The rest of the distillate is washed successively with strong sulphuric acid, water, caustic soda and water. The sulphuric acid removes the basic impurities, e.g., aniline and pyridine, and also some thiophene ; caustic soda removes carbolic acid. The washed light oil is then distilled using a fractionating column ; the distillate is collected in three fractions—namely, from 80-100°, 110-140° and 140-170° respectively. The first and second fractions are commercially known as '90 *per cent benzol*' and '50 *per* *cent benzol*' respectively—the term refers to the proportion of distillate which 100 c.c. of the commercial product yields on distillation below 100°. The 'fifty per cent benzol' contains about 46 benzene, together with some toluene and xylene. The third fraction is called **solvent naphtha** or **benzine** (consists mainly of xylene, etc.) and is used as a solvent for rubber, paints and resins, etc. The '90 per cent benzol, (which contains 70 per cent benzene, 24 per cent toluene and a little xylene) yields commercial benzene, toluene and xylene on careful fractionation. For further purification, the commercial benzene is cooled in freezing mixture, when pure benzene crystallise out. *Even then, it contains trace of thiophene, C_4H_4S.*

The presence of thiophene in coal-tar benzene may be shown by shaking a little of the benzene with a drop of concentrated sulphuric acid and a crystal of isatin, when a deep blue colour of *indophenin* is produced. No such colour is given by benzene made from benzoic acid.

Thiopene may be removed from coal-tar by agitation with small amounts of cold concentrated sulphuric acid.

Benzene, toluene and xylene are commercially known as benzol, toluol, and xylol respectively.

Benzene, C_6H_6, is the simplest of the aromatic compounds. It was discovered by Faraday in 1825 in the illuminating gas made from whale oil. It was isolated from coal tar by Hofmann in 1845. Bertholet first synthesised it in 1870 by passing acetylene through a red-hot tube. $3C_2H_2 = C_6H_6$

Commercial benzene is obtained from the light oil fraction of coal tar.

It can be made in the laboratory by distilling benzoic acid or its salt (sodium or calcium benzoate) with soda lime (*cf.* preparation of methane).

Experiment.—Mix sodium benzoate with twice its weight of sodalime, and distil the mixture from a retort attached to a condenser and receiver. Wash the oily distillate (smelling strongly of benzene) with water in a tap-funnel, dry with anhydrous calcium chloride and re-distil.

$$C_6H_5COONa \text{ (sodium benzoate)} + NaOH = C_6H_6 + Na_2CO_3.$$

Benzene is also obtained by distilling phenol with zinc dust

$$C_6H_5OH + Zn = C_6H_6 + ZnO.$$

Properties of benzene.—Benzene is a colourless liquid (b.p. 80.4° and m.p. 5.4°) with a peculiar but not unpleasant smell. It is very inflammable and burns with a smoky flame. It is lighter than water (sp. gr. 0.874 at 20°) and is insoluble in it, but is miscible with alcohol, ether, and petrol. It readily dissolves fats, resins, sulphur, phosphorus and iodine.

The chemical properties of benzene are typical of aromatic hydrocarbons and are often called *aromatic properties*. These include (i) *Resistance to oxidation.*—Benzene is a remarkably stable compound and resists oxidation by chromic acid or acid potassium permangante.

(ii) *Halogenation*—substitution of hydrogen by chlorine or bromine. Substitution takes place in presence of a catalyst (halogen carrier) such as iron powder or iodine. Halogenated products contaning from one up to six atoms of halogen are obtained.

$C_6H_6+Cl_2 = C_6H_5Cl$ (monochloro benzene) $+HCl$.

$C_6H_5Cl+Cl_2 = C_6H_4Cl_2$ (dichloro benzene) $+HCl$, and so on.

(iii) *Nitration*—substitutin of hydrogen by the nitro group, $-NO_2$. Benzene reacts with concentrated nitric acid in presence of strong sulphuric acid, forming nitrobenzene—the sulphuric acid absorbs the water formed in the process. Dilute nitric acid has no action upon benzene.

$C_6H_6+HO.NO_2= C_6H_5NO_2$ (nitrobenzene) $+H_2O$.

(iv) *Sulphonation*—substitution of hydrogen by the sulphonic acid group, $-SO_3H$. Concentrated sulphuric acid, on warming, dissolves benzene forming benzene sulphonic acid.

$C_6H_6+HO.SO_3H = C_6H_5.SO_3H$ (benzene sulphonic acid) $+H_2O$.

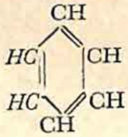
(v) **Friedel-Crafts reaction**—introduction of an alkyl or acyl group into the benzene nucleus in presence of anhydrous aluminium chloride.

$C_6H_6+C_2H_5Br = C_6H_5.C_2H_5$ (ethyl benzene) $+HCl$.

$C_6H_6+CH_3COCl = C_6H_5.CO.CH_3$ (phenyl methyl ketone) $+HCl$.

Sulphonation, nitration, and Friedel-Crafts reaction distinguish aromatic hydrocarbons from the aliphatic.

Unlike the aliphatic compounds which are *open chain* compounds, the aromatic hydrocarbon benzene possesses a *closed chain* or *ring* of six carbon atoms. Benzene has a regular hexagon formula with alternate single and double bonds. The famous German chemist Kekule (1829-1896) suggested the hexagonal formula for benzene in 1865.



Benzene contains three double bonds in a closed ring, and forms additive compounds with hydrogen, chlorine and bromine.

(vi) In bright sunlight benzene reacts with chlorine or bromine, giving benzene hexachloride, $C_6H_6Cl_6$ or benzene hexabromide, $C_6H_6Br_6$. It is reduced to cyclohexane, C_6H_{12}, by hydrogen in presence of finely divided nickel at 160°.

$$C_6H_6+3Cl_2 = C_6H_6Cl_6 \text{ ; } C_6H_6+3H_2 = C_6H_{12}.$$

Benzene reacts with ozone, forming a triozonide, pointing to the presence of 3 double bonds in it.

$C_6H_6+3O_3 = C_6H_6(O_3)_3$ (benzene triozonide).

(vii) *Failure to respond to the usual tests for unsaturation.*—In spite of 3 double bonds in benzene, it is very unlike the olefines, and in marked contrast *benzene reacts neither with bromine water nor with a solution of potassium permanganate in the cold*, the reagents which readily attack the olefines. Benzene also forms no addition compounds with halogen acids or strong sulphuric acid (*cf.* olefines). Benzene, therefore, possesses a peculiar degree of unsaturation.

Tests.—(i) Benzene burns, on ignition, with a smoky flame.

(ii) Benzene forms nitrobenzene (having a pleasant smell like that of bitter almonds) on being shaken with a mixture of concentrated nitric and sulphuric acids—on pouring the mixture in excess of water nitrobenzene separates at the bottom as a heavy pale yellow oil.

Uses of benzene.—Benzene is used : (i) as a solvent for oils and fats, (ii) for dry cleaning, (iii) for motor fuel, and (iv) for making nitrobenzene, and the insecticide *gammexane*, $C_6H_6Cl_6$.

QUESTIONS

1. What are hydrocarbons ? Give examples. What is the chief source of methane ? How is it usually prepared and purified in the laboratory ? Mention its important properties and uses. What happens when methane is led over a layer of red-hot cupric oxide ?

2. What is meant by unsaturation ? How is unsaturation detected in an organic compound ? Describe the preparation of a pure sample of ethylene in the laboratory ? Mention its chief properties and uses. What is the action of ozone on ethylene ?

3. How is acetylene prepared and purified in the laboratory ? State its properties, tests and uses. Explain what happens when it is led into (i) a jar of chlorine, (ii) hot dilute sulphuric acid containing mercuric sulphate, (iii) ammoniacal cuprous chloride solution, and (iv) a red-hot tube. *P. U.* 1961

4. Compare the properties of methane, ethylene and acetylene. How are they detected in a mixture and separated from each other.

5. Explain what happens when :
   - (a) sodium acetate is heated with soda lime,
   - (b) ethylene bromide is heated with zinc dust,
   - (c) cuprous acetylide is boiled with potassium cyanide solution,
   - (d) ethylene bromide is heated with alcoholic potash,
   - (e) ethyl alcohol is passed over heated alumina.

6. Describe the preparation and purification of chloroform in the laboratory. Mention its chief properties, tests, and uses. What precautions are taken to store it and why ? How would you test the purity of a sample of chloroform ? *P. U.* 1961

7. Explain what is meant by alcoholic fermentation. Outline the steps of making ethyl alcohol from starch by the process of fermentation. Mention the chief properties, tests and uses of ethyl alcohol. How may ethylene be converted into ethyl alcohol ?

8. (i) What is methylated spirit ? Mention its uses.
   (ii) How would you separate acetic acid from ethyl alcohol ?
   (iii) How is ethyl alcohol distinguished from acetone ?
   (iv) Explain the reactions of ethyl alcohol with : (a) sodium, (b) chlorine, (c) phosphorus pentachloride, (d) acetic acid, (e) sulphuric acid, (f) bleaching powder. What happens when ethyl alcohol vapour is passed over heated copper ?

9. Describe the preparation of a sample of acetone, starting from acetic acid. Compare its chemical properties with those of acetaldehyde. Mention the uses of acetone.

10. (a) How would you prepare : (i) acetaldehyde from acetylene (ii) acetone from ethyl alcohol, (ii) chloroform from acetone, (iv) acetaldehyde from acetic acid ?
   (b) By what pratical tests would you distinguish between acetaldehyde and acetone.

11. What are aldehydes and ketones ? Mention the typical reactions of the carbonyl group, as shown by the chemical properties of acetaldehyde and acetone.

12. Explain what happens when : (*a*) calcium acetate is heated alone, and in presence of calcium formate, (*b*) acetaldehyde is treated with potassium carbonate

solution, (*c*) strong sulphuric acid is added to acetone, (*d*) acetone is shaken with a saturated solution of sodium bisulphite, (*e*) ethyl alcohol is distilled with potassium dichromate and sulphuric acid ?

13. How is acetic acid prepared from pyroligneous acid ? Mention its chief properties, tests, and uses. How may acetylene be converted into acetic acid ?

14. Describe the 'quick vinegar' process of making acetic acid. Starting with acetic acid, how would you obtain : ethyl acetate, ethyl chloride, acetic anhydride, acetone and acetamide ?

15. What is an ester ? How is ethyl acetate prepared in the pure state in the laboratory ? Mention its chief properties, and uses. What happens when ethyl acetate is treated with : (*a*) caustic soda solution, (*b*) sodium and alcohol ?

16. What is the principal source of oxalic acid ? How is it obtained from it ? Mention its chief properties, tests and uses. Describe the action of : (*a*) heat, (*b*) conc. sulphuric acid, (*c*) potassium permanganate solution acidified with dilute sulphuric acid, (*d*) phosphorus pentachloride, on oxalic acid.

17. Outline the preparation of citric acid from : (*a*) lemon juice, (*b*) molasses. Mention its chief properties, tests and uses.

18. (*a*) What is the chief source of benzene ? How is it obtained from it ? Mention its principal properties, tests and uses.

(*b*) How would you obtain benzene from : (*i*) benzoic acid, (*ii*) phenol ? What is the common impurity in coal-tar benzene ? How is it removed to get pure benzene ?

(*c*) Explain what happens when methane and benzene are *separately* treated with : (*i*) concentrated nitric acid, (*ii*) bromine, (*iii*) hydrogen in presence of a catalyst, (*iv*) hot concentrated sulphuric acid ? Calcutta, 1959.

Measurements

The C. G. S. system.—The metric system is commonly adopted as the system of weights and measures in all scientific work. In this system, (i) the unit of length is the centimetre, (ii) the unit of mass is the gramme, and (iii) the unit of time is the second. Hence it is called C.G.S. or centimetre-gramme-second system.

The unit of lenth.—The *centimetre* (cm.) is one hundredth of a metre which is the exact distance between 2 marks on a standard bar of platinum at 0°C, preserved in Paris.

The unit of area.—The *square centimetre* (sq. cm.) is the area of a square of one centimetre side.

The unit of volume.—The *cubic centimetre* (c.c.) is the volume of a cube of one centimetre side. But the unit of volume or capacity often used is the *litre* which is *the volume of one kilogram of water at its maximum density at* 4°C. The litre was originally intended to be equal to 1 cubic decimetre, i.e., 1000 cubic centimetre. But 1 litre is now known to be equal to 1000.028 c.c. One *millilitre* (ml.) is one-thousandth of a litre, i.e. 1 ml. = 1.000028 c.c.

The unit of mass.—*Gram* or *gramme* is the mass of one cubic centimetre of water measured at 4°C, the temperature of maximum density. But this mass is now known to be 0.999,973 gram, i.e., 1 gram is the mass of 1.000028 c.c. of water at 4°C.

The unit of time.—The *second* is 1/86400th part of a mean solar day.

The normal or standard pressure.—This is defined as the pressure due to a column of mercury 76 cms. high at 0°C, at sea-level and latitude 45°, and is equal to $(76 \times 13.596 \times 980)$ or 1.013×10^6 dynes per square centimetre (density of mercury = 13.596, and gravitational constant = 980) = 14.7 lbs. per sq. in.

In metric system the prefixes *deci- centi-* and *milli-* are used to denote the fractions one-tenth, one-hundredth, and one-thousandth, while the prefixes *deca-*, *hecto-* and *kilo-* denote 10, 100, and 1000 times respectively.

1 metre (m.) = 10 decimetres = 100 centimetres (cm.) = 1000 millimetres (mm.)
1 gram (gm.) = 10 decigrams = 100 centigrams = 1000 milligrams (mg.)
1000 gms. = 100 decagrams = 10 hectograms = 1 kilogram (kg.)
1000 m. = 100 decametres = 10 hectometres = 1 kilometre (km.)

Conversion table of units

Length : 1 m. = 39.37 in. = 3.2809 ft. = 1.0936 yd. ; 1 kilometre = 0.621 mile.
1 in. = 2.54 cm. ; 1 ft. = 30.48 cm. ; 1 yd. = 0.9144 m. ; 1 mile = 1.609 km.

Volume : 1 litre ($l.$) = 1000 millilitres (ml.) = 1000 c.c. ; $1 l.$ = 1.76 pint.
1 cu. in. = 16.387 c.c. ; 1 cu. ft. = 28.32 $l.$; 1 gallon = 4.546 litres.
1 gallon of water = 0.1605 cu. ft. = 4.546 $l.$; weighs 10 lbs.
1 cu. ft. of water at 62°F weighs 62.3 lbs. ; $1l$ of water = 1000 c.c. ; weighs 1 kg.

Weight : 1 lb. = 16 oz. = 7000 grains = 453.59 gms. = 0.45359 kg.
1 kg. = 1000 gm. = 2.202 lbs. = 0.001 metric ton = 85.7 tolas.
1 gm. = 0.035 oz. = 15.43 grains ; 1 oz. = 28.35 gm. ; 1 grain = 0.065 gms.
1 ton = 27 maunds nearly ; 1 stone = 14 lbs.

Apothecary's unit—1 c.c. = 0.033 ounce = 0.27 dram.
1 ounce = 29.57 c.c.s. ; 1 dram = 3.7 c.c.s.

Temperature : $°F = \frac{9}{5}\ °C + 32$; $°C = \frac{5}{9}\ (°F - 32)$.

CALCUTTA UNIVERSITY PRE-UNIVERSITY CHEMISTRY SYLLABUS

ONE PAPER

Theoretical—100 marks.

General : (i) Common laboratory processes : filtration, crystallisation, sublimation, distillation, solution, solubility, true solution and colloidal solution (elementary ideas).

(ii) Physical and chemical changes, law of conservation of mass. Laws of chemical combination by weight. Dalton's atomic theory.

(iii) Avogadro's law, simple deductions (M = 2d, diatomicity of elementary gas molecules), derivation of formulae from composition for water, hydrogen chloride, and carbon dioxide.

(iv) Atomic weight, molecular weight, gram molecule.

(v) Symbol, formulae and equations, *simple calculations on weights and volumes.*

(vi) Ionic dissociation, electrolysis, Faraday's laws, simple calculations on $w = czt$.

(vii) Brief but broad outline of atomic structure : proton, electron, neutron, atomic number.

(ix) Acids, bases and salts, acidimetry and alkalimetry, simple problems.

Non-metals : (i) Laboratory preparation of oxygen, hydrogen, nitrogen, carbon dioxide ; their main properties and uses.

(ii) Oxidation and reduction ; one method of preparation of hydrogen peroxide ; its properties and uses.

(iii) Catalysis, allotropy referred to oxygen, carbon and sulphur (names only).

(iv) Ammonia—laboratory preparation, outline of Haber's method, properties, uses ; Nitric acid—preparation from nitrate, from ammonia (outline only), action on sulphur, sulphur dioxide, magnesium, zinc, and copper, properties of aqua regia.

(v) Phosphorus—two main forms, their properties; their uses—outline of preparation of phosphoric acid and phosphorus from bone ash.

(vi) Laboratory preparation of chlorine, bromine, and iodine; their common properties; uses. Preparation of hydrochloric acid in the laboratory; properties.

(vii) Sulphuretted hydrogen—laboratory preparation; reducing property, uses as a reagent; sulphur dioxide from sulphur burning; outline of manufacture of of sulphuric acid by contact and chamber process (only raw materials, equations and conditions to be stated). Uses of sulphur dioxide and sulphuric acid. Alum—potash alum and its uses.

Chemistry of carbon compounds: (i) Destructive distillation of coal and wood, only names of products and their uses.

(ii) Hydrocarbons: saturated—methane; unsaturated—ethylene, acetylene; aromatic—benzene, only source, outline of preparation with equation, important reactions and uses.

(iii) One simple method of preparation; main properties and uses of the following classes of organic compounds with special reference to the compounds noted against each: (*a*) alcohol—ethyl alcohol, (*b*) aldehyde—acetaldehyde, (*c*) ketone—acetone, (*d*) carboxylic acid—acetic acid, oxalic acid, and citric acid, (*e*) esters—ethyl acetate, (*f*) halogen derivatives—chloroform.

Metals: (i) Occurence, outline of extraction without technical details, properties and uses of zinc, aluminium, sodium, and iron.

(ii) Preparation (in outline) and uses of: (*a*) Solvay's sodium carbonate, (*b*) caustic soda (Castner's), (*c*) lime, (*d*) bleaching powder, (*e*) copper sulphate, (*f*) plaster of Paris.

Practical syllabus: (i) Fitting up of a simple apparatus, *e.g.*, a wash-bottle.

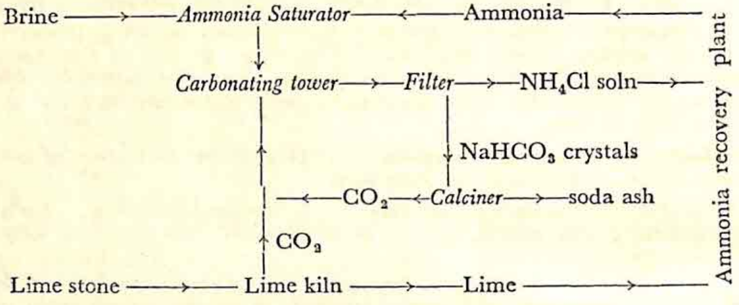
(ii) Separation of ingredients of a solid mixture by solution, filtration, crystallisation and sublimation.

(iii) (*a*) Preparation and study of properties of oxygen, carbon dioxide, ammonia; (*b*) study of the action of sulphuretted hydrogen on different salt solutions.

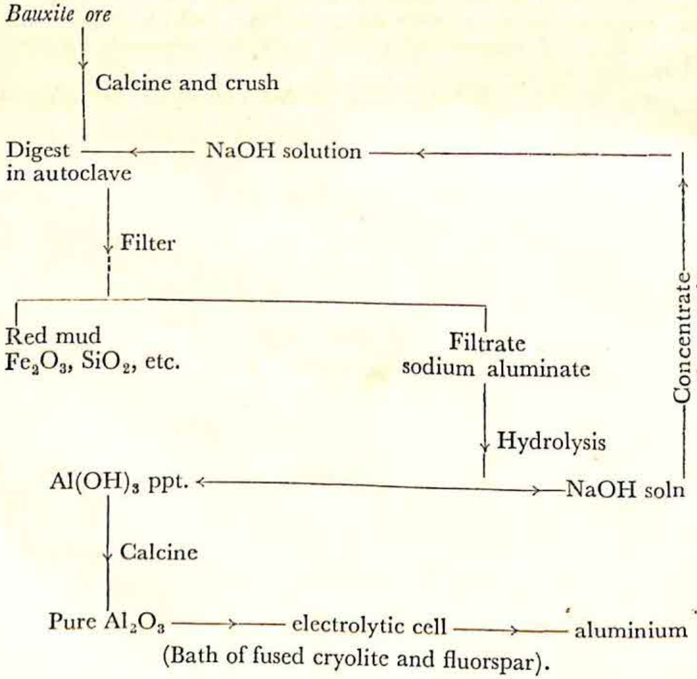
(iv) Identification of (*a*) acid radicals (chloride, carbonate, nitrate and sulphate) in sodium, potassium or ammonium salts, (*b*) basic radicals (copper, aluminium, iron, zinc, calcium and magnesium) given singly in compounds soluble in water or dilute hydrochloric acid.

(v) Titration of acid and bases using methyl orange or phenolphthalein as indicator.

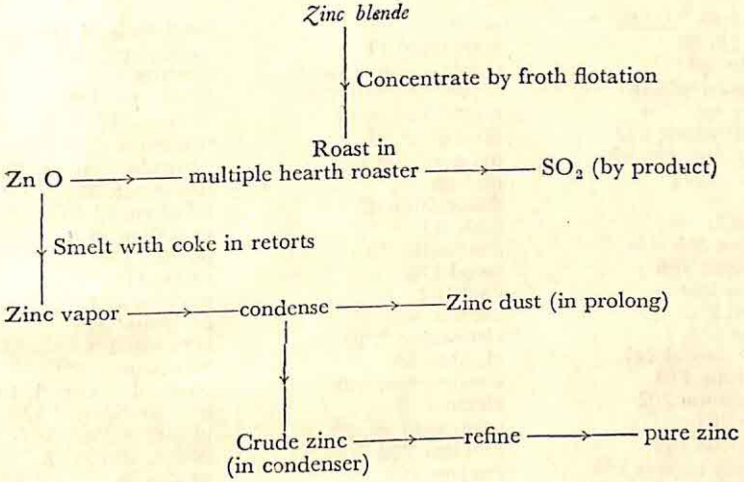
Flow sheet of soda ash preparation by the Solvay process



Flow sheet of extraction of aluminium

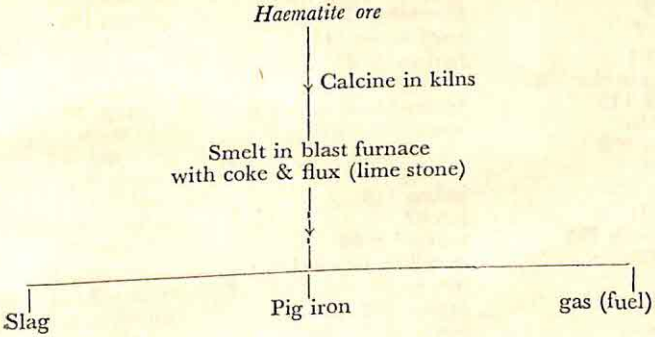


Flow sheet of extraction of zinc



Zinc blende
Concentrate by froth flotation
Roast in multiple hearth roaster
Zn O
SO$_2$ (by product)
Smelt with coke in retorts
Zinc vapor
condense
Zinc dust (in prolong)
Crude zinc (in condenser)
refine
pure zinc

Flow sheet of extraction of iron



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